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NIAGARA FALLS MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY

The fourth general meeting of the American Electrochemical Society, a full report of which is found in this issue, again scored a full success, and will be remembered by all who attended it as a highly profitable and enjoyable affair. True, both the attendance and the number of papers fell short of the figures reached in the last two meetings, but this was only what was to be expected. The first three meetings, at Philadelphia, Niagara Falls and New York City, represented a series of successes, each greater than the former, so that some moderation in the pace was inevitable. The fact that this only manifested itself in a quantitative but not in qualitative respect, speaks very well for this youngest of the technical societies of this country. Good will and good feeling all around were the keynote of the social features of the meeting, and that the numerous workers in the art and science of electrochemistry who only two years ago were absolutely scattered, and without any connecting link, are now firmly bound together in professional solidarity is probably the most important broad result to be credited to the society.

While the slight decrease in the number of papers presented to the society will somewhat curtail the thickness of the printed volume of the Transactions, yet the members who attended the sessions were, perhaps, pleased that the technical programme was not overcrowded to the same degree as at the last two meetings, and that there was thus allowed time for thorough discussion of the papers presented. An important feature was the comparatively large number of papers on practical subjects, and it is noteworthy that some of the best papers of this class came from American universities.

An excellent example of what scientific investigations in our universities can do for the progress of industry was Dr. Bancroft's paper. We do not think its intrinsic value is to be found entirely in the three suggestions formulated at the end of the paper, but rather in the exact and systematic method of determining accurate numerical data on the mutual relation between current density, temperature, and power consumption in copper refining. The tables of cost and the conclusions reached as to the conditions under which the cost becomes a minimum, are of value as showing how to apply the results of systematic scientific work to certain given conditions of practice. Dr. Bancroft has clearly stated the conditions for which his results are true, and has given both the items of cost which he has taken into account and those which he has not. Every copper refinery knows exactly all the conditions under which it is working, and is now able to determine the most economical current density and temperature for its own case on the basis of Dr. Bancroft's experiments. Of special interest is Dr. Bancroft's recommendation as to covered tanks, which did not

meet with the approval of several prominent practical refiners who joined in the discussion. But this question, as Dr. Bancroft remarked, is one that should be considered purely a question of cost. He gives the data, showing how many dollars and cents can be saved in power by the introduction of covered tanks, and the question to determine is whether this saving in cost is counterbalanced by increase in cost in other directions. If we consider the high degree of perfection of the mechanical features of our modern refineries, we should think that a convenient method of mounting the covers, and one which would allow an easy inspection of the tanks, is not impracticable.

Prof. Brown's paper on the nickel deposition also was of great interest. We have frequently urged in this journal that electroplaters should endeavor to know what is going on in their cells, and that in order to get good results they should not only consider the cathodic deposit, but the actions in the cell as a whole. The fundamental point which decides the success of any electrolytic process, namely, that the initial conditions should, so far as possible, be maintained during the entire process of electrolysis, requires in the case of the plating bath that the anodic corrosion shall correspond to the cathodic deposit. The ideal method of ascertaining whether this is the case is naturally Prof. Brown's method of measuring the anodic potential against a standard electrode; but human inertia is also a law of nature, and it seems too extravagant a hope to entertain that the average electroplater will readily be brought to measure electrode potentials in this manner. However, the test suggested at the end of Prof. Brown's paper appears to be a good substitute, and requires little apparatus. At least a good voltmeter should certainly be in the hands of every electroplater.

Prof. Burgess' paper on an electrolytic method of removing brass from iron is a very pretty example, showing how well-known old facts which are apparently only of theoretical interest may be used in actual practice. On Dr. Walker's paper on the cathodic reduction of gold ores we comment in another editorial note. From Mr. Salom's paper it appears that while the chemistry of his lead reduction process has not been changed, yet his new cell involves a great improvement in mechanical features. Mr. Hambuechen's paper related to an interesting cell which, by means of an aluminium electrode used as an electrolytic valve, acts at the same time as a rectifying and as an electrolytic cell. Finally, Dr. Byrnes' paper was a very welcome contribution to the extremely important question how to construct a good diaphragm for certain classes of electrolytic work.

While most of the practical papers thus concerned some phase of electrolytic work, there were two interesting papers on the subject of electric furnaces. Mr. FitzGerald gave some general rules for the design of resistance furnaces, and Mr. Ruthenburg recorded the latest advances of his promising electric iron process. Of the papers on theoretical problems, that of Mr. Moltkehansen was an interesting example of the application of electric methods to the decision of doubtful chemical problems. The paper of Dr. Richards and Mr. Landis was of special interest on account of the apparently bold suggestion of a method of measuring electric conductivities of solutions by a direct-current method. Mr. Lidbury's paper proved again how dangerous it is to make generalizations based merely on some similarity between different classes of phenomena; his very interesting results on the electrolysis of water vapor, due to electric spark discharges, should call the attention of more experimenters to this important field. The general discussion of the electrolytic dissociation theory was rather tame, in view of the savage opinions held by some on one side or the other of this polemical question. Two points brought out in this discusion were of special interest. First, Dr. Bancroft's claim that the experimental investigations of the past are not sufficient to establish the molecular weights in solutions as abnormal, and that accurate investigations on this fundamental question are under way. Second, Dr. Richards' interesting paper on the thermochemistry of the dissociation theory, with his peculiar method of calculating the neutralization heat. We hope to return to this subject in a later issue.

THE GENERATION OF ACETYLENE

The future of the calcium carbide industry depends essentially on the progress of the use of acetylene for lighting, and consequently the problem of generating acetylene from calcium carbide and water is one of prime importance. At first sight the problem is an extremely simple one. Whenever calcium carbide is brought into contact with water, the generation of acetylene results. That this apparent simplicity has been an enormous incentive for inventors, seems to be indicated by the fact that there have been granted about 1000 United States patents for acetylene generators. On the other hand, promoters were equally attracted, and in Europe, wherever there was a small water-power, it was considered as a suitable place for erecting a calcium carbide plant. The large European manufacturers of electrical apparatus fostered this ultra-rapid development, interested, however, rather in the sale of electrical machinery than in the permanency of the calcium carbide business. Overproduction and a general commercial crash in the European calcium carbide industry was the natural result.

We may point with some pride to the fact that in this country of "unlimited possibilities," the calcium carbide industry has developed along conservative lines, has shown a slow but steady growth, and gives every promise of continuing to develop along the same lines. This is essentially due to two reasons: First, the calcium carbide industry is in this country in the hands of a single large and responsible company—which example indicates that monopoly may at times be a very useful thing for all concerned; and, second, the careful examination of acetylene apparatus by a committee of the National Board of Fire Underwriters, which has issued a "list of permitted machines." It is now clearly understood that the problem of the generation of acetylene from calcium carbide and water is a chemical problem, and that the designer of an acetylene apparatus must not only possess mechanical skill, but a knowledge of the chemistry of the subject.

We are glad to call the attention of our readers to an article contributed to our present issue by Mr. J. M. Morehead, who, as the chemist of the Union Carbide Co., speaks

with authority on this subject. Electrochemical methods may be considered generally as a means for storing energy in form of a chemical compound; and, in fact, this is the only effective means, known up to the present, for storing energy. The energy of the falls of Niagara, after conversion into electrical energy, is stored in form of chemical energy in calcium carbide. We get the energy back when we change calcium carbide into acetylene and use acetylene for lighting. When acetylene is used for illumination somewhere in the West, we have a case of chemical transmission of energy from Niagara to the West. Calcium carbide is an exceedingly active chemical substance, which property gives it its commercial value, but, as Mr. Morehead points out, this same property has to be reckoned with in obtaining the maximum degree of satisfaction and safety in its use. A careful and scientific study of the physical chemistry of the process of generating acetylene has led to the understanding of three possible sources of danger; danger from overheating, from excessive after-generation, and from an explosure of a mixture of gas and air. Mr. Morehead's discussion of these three points, and of the means by which danger has been eliminated in the modern design of acetylene generators, is very lucid, and should appeal, not only to chemists, but to the large class of progressive engineers in several fields who may have to consider the installation of acetylene generators, but are not yet convinced of their practical safety. As such progressive engineers are largely represented in the subscription list of this journal, we hope that Mr. Morehead's article will do some good. There can be no doubt that in great sections of this country where electric light installations would not pay, acetylene will be the illuminant of the future, and is entitled to this role by the excellence of its light per se.

THE PRECIPITATION OF GOLD FROM CYANIDE SOLUTIONS.

In this issue we publish an interesting paper on the precipitation of gold from cyanide solutions by Messrs. W. A. Caldecott and E. H. Johnson. The long activity of the authors in the classical country of cyanide processes—in South Africa—gives special weight to their exposition of the problem which is not only of the greatest commercial importance, but also of much scientific interest on account of the complex, and not yet fully understood chemical reactions involved in this process. Practically we distinguish between the precipitation of the gold by means of the electric current, as in the Siemens & Halske process, and the so-called chemical method of precipitation by means of zinc shavings or zinc dust. But from the facts recorded by Messrs. Caldecott and Johnson one might conclude that this latter "purely chemical" method is also essentially an electrochemical process. The authors record the fact that the precipitating efficiency of chemically pure zinc is almost nil, impurities in the zinc being essential. This fact would lead to the hypothesis that when we use zinc shavings we have short-circuited galvanic cells, the pure zinc and the impurities acting as electrodes respectively.

However, the electric precipitation of gold from a cyanide solution upon the cathode is not a very simple affair. We know that gold is not the cation of the double salt of gold and potassium, but that it represents a part of the anion radicle, which, under the directive force of the current, moves away from the cathode. Potassium is the cation and is primarily deposited on the cathode, and the cathodic deposition of gold which we observe is only the result of a secondary reaction between the primarily deposited potassium and the double salt in solution. This explains why thorough agitation of the solution is an essential element of success.

In this connection we may refer to a method of precipitation of gold from certain telluride ores, described by Dr. W. H. Walker in an American Electrochemical Society paper, read at Niagara Falls and abstracted on another page of this issue. Dr. Walker found that with the special type of ore with which he experimented, the gold deposit on the cathode was due to direct cathodic reduction rather than to a previous anodic solution and following cathodic deposition. Dr. Walker's method is therefore essentially different from the Siemens & Halske process. While the latter may be compared in some respects with the process of copper refining, involving first solution and afterwards precipitation, Dr. Walker's method is analogous to the Salom process of cathodic reduction of galena to lead.

ELECTROLYTIC PRODUCTION OF DYES AND PIGMENTS.

Aside from the electrolytic production of white lead, the discussion of patents relating to which is completed in the digest of the present issue, the United States patents cover a variety of dyes and pigments produced by electrolytic methods. The organic dyes are but scantily represented, the patents being confined to a few simple reduction and oxidation methods. In the production of pigments, however, we find a considerable number of variations of a single principle. In general, a soluble anode is dissolved in a suitable electrolyte, and the desired compound of the anode metal is precipitated, either by the hydroxide, which is simultaneously produced at the cathode, or by a suitable precipitant added to the electrolyte. Thus, for instance, hydrated copper oxide is produced by solution of a copper anode in sodium chloride solution and subsequent reaction with the caustic soda from the cathode; basic phosphate of copper is produced by the electrolytic solution of copper anodes in chlorate solutions to which soluble phosphates are added; lead chromate results from the passage of the current from a lead anode through an electrolyte consisting of soluble chlorates and chromates, etc.

Whatever advantage this method is presumed to possess over direct precipitation of the compound from mixed solutions obtained by ordinary chemical methods must be based upon the assumption that the current efficiency is substantially perfect; otherwise very serious difficulties arise, because the current losses will be found to correspond quite closely to changes undergone by the electrolyte, and such changes mean in general, not only a variable product, but an excess of acid or alkali, the effect of which is to introduce very serious disturbances. Such effect seems moreover to be cumulative, so that variations from the theoretical efficiency which might appear at first sight to be negligible may have a serious bearing upon the question of practicability. The value of such methods is only to be determined after long-continued trials.

METALLURGY AND CHEMISTRY IN SOUTH AFRICA

The Chemical, Metallurgical and Mining Society of South Africa held its general meeting on July 18, in Johannesburg. The proceedings of the meeting are recorded in the July number of the journal of the society.

Mr. S. H. Pearce, in his presidential address, referred to the beginning of the society, when it was nicknamed the Cyanide Club; "considering the vast improvements made in the cyanide process, mainly by efforts of the members of the society, it is a matter rather to be proud of than otherwise." He referred to the many possibilities which have sprung up since the late war, and expressed the hope that South Africa will soon respond to the attack that combined capital and labor are making upon its resources, and will become not only self-supporting, but take that prominent part in contributing to the world's supply of metals, minerals and even foodstuffs, that it does now in the supply of gold and diamonds.

After some remarks on mining problems which have sprung up, Mr. Pearce remarked that if one looks up the metallurgy of gold, one finds that in the early days of Australia the first mining was limited to washing up alluvial ground; later it was found payable to hand-crush the richer quartz and pick out the nuggets, long before the introduction of stamp mills and amalgamation. So it is in South Africa; so long as there is so much apparent profit in it, gold mining will remain the staple industry; but now the country is being thoroughly prospected, and it will not be long before those deposits, which are at present only indicated, will be definitely located, and the production of other metals become an accomplished fact. Large deposits of iron ore, of a higher class than many being worked in Europe or America, are known, and in some cases in proximity to coal, clay, lime, etc. Copper, zinc, nickel, lead, silver, tin and antimony are known to exist in varying quantities, as also are oil shale areas, while the coal deposits, if not always of a very high quality, appear to be unlimited, and will possibly be supplying the world when all others are exhausted.

South Africa, Mr. Pearce says, is backward in the chemical field. There is at Modderfontein a dynamite factory, one of the finest of its class, and there is also a chemical works, whose chief product is sulphuric acid, but beyond this, chemical industries are practically wanting. In agricultural chemistry very little has been accomplished; hygienic chemistry is another subject practically untouched.

"Analytical chemistry is a matter that more directly concerns us, and in this matter, including, as it does, the assaying of ores, tailings, and residues, etc., I should like to bring to your notice and consideration the plan of standardizing methods of analysis, as in America, by means of commissions appointed to determine those which are best and most suitable, these being subsequently adopted as standard methods throughout the country. If we take as an example our methods of assaying and sampling, the matter will appeal to most of you. Comparisons are always odious, but we have got into the habit of making them frequently in the matter of extractions, and as there is probably no other place where minute accuracy is of the same importance as it is in this matter, I have no hesitation in stating that up to the present we have still much to do before our comparisons are justly based. There is no reason why we should not appoint our own commissions and show that we can also evolve standard methods here just as we have been able to pioneer the way in the cyanide process of gold extraction."

Mr. W. Cullen remarked that while South Africa metallurgy in the past has been exclusively gold, yet he does not think that it will be very long before they have one or two other metals, such as lead and zinc, to deal with.

Mr. H. S. Denny read a paper with the title "Observations on the Metallurgical Practice of the Witwatersrand." An abstract of this paper, which was characterized by the president as "the most interesting paper ever read before the society," will be published in our next issue. The following papers were read by title: "An Automatic Pulp Sampler," by James Higham; "The Ventilation of Deep Levels," by Thomas Johnson; "The Precipitation of Gold from Cyanide Solutions," by W. A. Caldecott and E. H. Johnson. The last paper is published, nearly in full, elsewhere in this issue.

MINERAL RESOURCES OF CUBA.

From the recently published annual report of the United States Consul-General at Habana for 1903 we gather the following information concerning the mineral resources of Cuba.

There is not at present sufficient knowledge regarding the real mineral richness of the island to form an exact opinion or to make an accurate estimate of the same. In former times, the mines were profitably worked. The industry afterwards was totally stopped, owing to the abnormal circumstances in which the island remained during many years. The benefits of peace are giving new vigor to this enterprise, judging from the great number of petitions for concessions filed in the offices of the civil governors of provinces.

The mineral resources of the island are represented by the following products: Gold, silver, iron, copper, manganese, lead, asphalt, petroleum, naphtha, graphite, amianthus, zinc, mercury, and, it is stated, coal. These minerals are found in most of the provinces, but the richest mineral district is the province of Santiago de Cuba, followed in importance by Santa Clara, Puerto Principe, Pinar del Rio, Matanzas and Habana. The following statement of the existing mining concessions in the different provinces will give an idea of the importance of the mineral interests of the island, and the list will be increased when exact and complete statistical data can be obtained:

Province	Mines Number.	Area. Acres.
Santiago de Cuba	386	44,586
Santa Clara	59	4,288
Puerto Principe	27	5,202
Pinar del Rio	13	1,361
Matanzas	11	444
Habana	10	514
Total	506	56,395

Of this number of mines, very few of iron, manganese, and copper in the province of Santiago de Cuba are in operation. The others can be considered only as concessions waiting for funds for exploitation. The administration, according to the laws in force, can not compel the miners to operate their claims. The owner is in possession of his mine to perpetuity, and at his own will may work it or not. The only cause of forfeiture established by the law is the failure to pay the annual taxes.

The taxes to be paid to the government are $5 yearly per hectare (2.471 acres), or $30 for each claim containing 6 hectares (14.8 acres), when the mines are of precious stones or metalliferous substances.

In the other cases, the tax is $2 per hectare (2.471 acres).

THE NATIONAL BUREAU OF STANDARDS.

From a recently published report of the National Bureau of Standards, of which Dr. Stratton is president, it appears that the departments dealing with electricity, thermometry and pyrometry, are already in working condition. At present there are facilities in the electrical department for the comparison of resistances covering a wide range, and for the calibration of direct-current ammeters up to 600 amperes, direct-current voltmeters up to 300 volts and of direct wattmeters. The equipment of the alternating department is not yet complete. The department of thermometry is equipped with the necessary apparatus for measuring temperatures in the intervals from 0° to 100° C., with the highest attainable accuracy. For work between 100° and 550° C. apparatus is now under construction, and for the testing of pyrometers in the interval between 500° and 1500° C., much of the necessary apparatus is already in hand.

THE GENERATION OF ACETYLENE.

By J. M. Morehead.

Calcium carbide is an exceedingly active chemical substance. It possesses chemical and physical properties which give it its commercial value, but which at the same time have to be reckoned with to obtain the maximum degree of satisfaction and safety in its use. Carbide will evolve acetylene through the simple contact with water, but, on the other hand, it will continue to evolve acetylene as long as there is carbide in contact with water, and if confined the pressure will rise beyond the pressure necessary to liquify the gas, which is at ordinary temperature 750 pounds to the square inch, and the heat of compression and of generation will rise to a point higher than the dissociation temperature of the liquified acetylene. Acetylene will give from ten to twelve times the light of ordinary gas for the same volume, but at the same time, it possesses more than twice the heat units of the best water gas, and when mixed with just the proper proportion of air and ignited it, like water gas, will dissociate with explosive violence, the energy of the explosion being in proportion to the heat unit content.

When it is considered that the only thing necessary for the production of acetylene is the simple contact of calcium carbide and water, and that the necessary and inevitable result is the immediate evolution of quantities of acetylene varying only in direct proportion with the quantity and purity of the two bodies concerned in the reaction, it would seem that very little scope was afforded to the mechanical ingenuity of the inventor in devising means by which the necessary contact between the two interacted bodies can be brought about; but a glance through the patent files of the last five years, through the advertising columns of the trade journals or the list of over one hundred generators—all different—which have been passed by the various boards of underwriters will prove that such is by no means the case.

Unfortunately a number of designers of acetylene apparatus, while undoubtedly possessed of a high degree of ingenuity and mechanical skill, had but little idea and less definite knowledge of the properties of one of the bodies with which they were dealing, and as a result many generators were arranged with very little regard to safety, and while they did generate acetylene, they made the gas in anything but its purest form, and many gave a far smaller yield of gas of probably a lower candle power per unit of carbide consumed than could be gotten from the same carbide by some machine else constructed upon more rational principles. The weak points in the early designs soon made themselves evident by leaks, by unsatisfactory light, by high cost for light and, in some instances, by explosions.

As the different defects became known, they were corrected in the succeeding machines, and with the growth of the business, the smaller and more irresponsible manufacturers have been crowded out, until now, with the ninety-three thousand machines in actual operation, operated for the most part by people with a minimum of mechanical ability, and an absolute ignorance of gasmaking, an accident is of exceedingly rare occurrence, and in almost every case where one does occur, is directly traceable to the needless ignorance or to the gross carelessness of the person having the generator in charge.

A great part of the progress towards safety in the design and construction of acetylene apparatus has been due to the thorough and intelligent supervision given to all appliances by the underwriters board of engineers. This board inspect and test all apparatus with a view always first to safety, and then to efficiency and to economy, and until the apparatus has received their sanction, it is not allowed in insured buildings.

The three points most to be considered are danger from overheating, danger from excessive after-generation, and danger from an explosion of a mixture of gas and air.

So far as the toxic properties of the gas are concerned, they may be considered as practically zero. If nothing but acetylene was breathed for a sufficient time, death from asphyxiation would ensue just as would be the case if nothing but hydrogen or nitrogen or carbonic acid or steam were breathed, but in so far as being poisonous, that is in being able to arrest the processes of animal life, like cyanogen or the carbonic oxide contained in water gas and coal gas, is concerned, acetylene may be considered as absolutely safe.

Grehant reports that in his laboratory a dog breathed a mixture containing 20 per cent acetylene and 80 per cent of air for thirty-five minutes without showing signs of distress, while another dog breathing a similar mixture of coal gas and air containing only 1 per cent. of carbon monoxide, quickly showed convulsive movements and died after ten minutes. An ordinary sized bedroom, say 12 x 12 x 12 feet, contains 1728 cubic feet. Twenty per cent of this is 345.6 cubic feet. It would require the largest acetylene burner 346.6 hours, or 14.33 days to produce a 20 per cent mixture in this room, and the ordinary sized burner twice as long, and this is upon the assumption that there is absolutely no ventilation.

When we consider the strong odor which acetylene possesses, and which would give immediate warning of a leak, we may dismiss the fear of any danger of asphyxiation connected with acetylene, and if our cousin from the country prefers to blow out the gas, let him, it will do no harm.

Overheating.

When calcium carbide is brought into contact with water, a certain definite amount of heat is generated from the reaction of their mutual decomposition, and of the attendant subsequent slaking of the lime, which is produced as a by-product and left as a residue. There is no way of avoiding the production of this heat. It is in obedience to a law of nature. The ability to, and the necessity of, producing heat when brought into contact with water is one of the physical properties of calcium carbide just as weight, color or crystalline structure is. It cannot be avoided and so must be provided for. This heat amounts to 414.6 calories per gram of pure carbide, or one pound of pure carbide develops, when acted upon by water, sufficient heat to raise the temperature of 89.4 gallons of water, one degree F., or the temperature of one gallon of water 89.4° F. Or the heat, liberated by the evolution of gas from one pound of pure carbide and from the subsequent slaking of the lime forming the residue—provided that none of the heat were wasted—is sufficient to raise the temperature of 0.49 gallon of water from the freezing point to the boiling point.

The first consideration in the design of an acetylene generator is means of getting rid of this heat. At a temperature of 536° F., or about half the temperature of dull redness, acetylene polymerizes and changes in the chemical structure of the acetylene begin to take place, and the degree of success attained in keeping the temperature below the above point determines in a very large measure the success or failure of the machine.

There are two ways of getting rid of this heat of generation:

First, by dissipation into the surrounding air, and, second, by absorption in water.

Dry machines depend upon the first principal. Wet machines upon the second. A few small machines, bicycle and automobile lamps, etc., depend upon the first principle. All large machines upon the second. The underwriters require provision for one gallon of water for every pound of carbide, and as it requires only 0.56 of a pound or a little over one-half pint of water for the chemical reaction, the possibility of danger, or rather of annoyance from overheating, may be considered as out of the question with any approved acetylene generator now on the market.

Overgeneration.

As mentioned above, if care is taken and everything worked just exactly wrong calcium carbide and water are capable of

producing excessive pressure, but the present generators retain their gas by means of water seals, which would "blow" at a few pounds and relieve the pressure. They are all—with one exception—made of galvanized iron, which would rupture before a dangerous pressure was reached, and, too, the board of underwriters require that all approved machines be provided with automatic blow-offs, piped to the outside air. These blow-offs open automatically for either excess volume in the holder, or excess pressure any place in the system.

As acetylene is non-explosive up to very high pressure, this possible source of danger may be considered as provided for and safe-guarded.

Explosion of Mixture of Acetylene and Air.

A gas explosion is not, properly speaking, an explosion. It is really a very rapid and a very violent burning. A true explosion is a dissociation, a tearing apart, while a so-called gas explosion is the result of a combination. A true explosion, which results from the ignition of nitro-glycerine, gunpowder and the other nitrate explosives, gives rise to permanent gases which occupy vastly more space than did the original solid or liquid body concerned in the reaction. A cubic foot of gunpowder without any admixture of air or anything else, if heated to 400° F. will dissociate according to the formula,

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + N_2$$

into permanent gases, which, when cold, will occupy 280 cubic feet. The temperature attained at the instant of dissociation is 2100° to 2200° F., and as gases double in volume for an increase of 492° F. in temperature, gunpowder may be said to produce at the instant of explosion about 1200 its volume of gas.

A cubic foot of nitroglycerine, if heated to 350° F., dissociates according to the formula,

$$4C_3H_5N_3O_9 = 12CO_2 + 10H_2O + 6N_2 + O_2$$

into permanent gases, which, when cold will occupy 748 cubic feet. The temperature in this instance would be 4500° F., and the total volume of gas at the instant of explosion would be 6748 cubic feet, or as many times the volume of the original explosive.

As compared with these, acetylene at anything less than several hundred pounds pressure is not of itself explosive. It can be polymerized or caused to combine with itself, but no amount of heat or of concussion will cause it to dissociate into its elements. To get any explosive effects, acetylene must be mixed with just the right amount of air. The maximum explosive effect is obtained by mixing the gas with two and a half times its volume of oxygen or 12.5 times its volume of air. A mixture of acetylene and oxygen requires a temperature of 512° F. to ignite it when it combines according to the formula,

$$C_2H_2 + 5O = 2CO_2 + H_2O.$$

If mixed with 12.5 parts of air instead of with pure oxygen, the reaction is the same, except for the pressure of nitrogen on both sides of the equation. The nitrogen is not changed, but serves to raise the ignition temperature from 512° to 900° F. The temperature of combination of acetylene and 12.5 per cent of air, due to the fact that acetylene is an endothermic body is high, reaching the temperature of 4100° F.

One volume of acetylene and 2½ of oxygen give rise to only two volumes of a permanent gas, or one cubic foot of the explosive mixture produces .59 cubic feet of gas against 280 and 748 for gunpowder and nitroglycerine, respectively. The energy of a gas explosion is due to the sudden heating of the gases produced, and of the nitrogen carried by the air. This 2.86 volume of inert nitrogen to every one volume of active acetylene and oxygen in the mixture has a very great retarding effect upon the reaction, and hence the energy of the explosion is far less than would appear from a consideration of the temperature attained or which would be the case with pure acetylene and oxygen.

In a gas explosion, two things are essential. First, a mixture of gas and air in proper proportions. Second, the mixture must be ignited. There are two ways of avoiding an explosive mixture. First, not to supply sufficient air for combustion, and, second, to dilute the gas with air beyond the explosive point. Mixtures within these limits will combine with explosive violence if ignited. The explosive limits of the more common gases are as follows, the percentages are by volumes.

	Start		Maximum Explosibility		Stop	
	Gas	Air	Gas	Air	Gas	Air
	Per cent		Per cent		Per cent	
Acetylene	3.1	96.1	12.5	87.5	24.1	75.9
24 C. P. water gas	7.8	92.2	17.0	83.0	2.3	77.0
Pintsch gas	4.8	95.2	9.0	91.0	11.0	89.0
Natural	6.5	93.5	11.0	89.0	11.8	88.2

It will be noted that the limits for acetylene are wider than are those for the other gases. This is explained by the superior gravity of acetylene. There is more carbon and hydrogen, more substance, more *gas* in a cubic foot of acetylene than there is the other gases. This will be seen by an inspection of the following table of specific gravities:

	Gravity.
Air	1.00
Acetylene	0.92
24 C. P. water gas	0.64
Pintsch gas	0.73
Natural gas	0.56

The chances of getting a mixture of acetylene and air which will be within the explosive limits are less with this gas than with other gases. Taking the same bedroom mentioned above, the largest burner would have to be left open for almost eight days before a mixture of maximum explosibility would be obtained, and it would be over three days before the mixture could be lighted. This assumes also that there is absolutely no ventilation. Another point which makes for the safety of acetylene is the limited quantity available. So rich is the gas that the ordinary generator does not hold more carbide than sufficient to make about fifty feet of gas, and in case of a broken pipe or fitting, this is the maximum amount to be had. Having obtained the mixture which is within the explosive limits, it is still necessary to ignite it. There are two ways of doing this.

First, by heat of generation inside of the generator, and, second, by heat or flame from outside.

While it is a chemical possibility to obtain sufficient heat to ignite acetylene by slowly and continuously adding water to a large excess of carbide, the modern machines, which drop a limited quantity of carbide at a time into a large excess of water, have almost entirely eliminated this possibility of danger.

The generators now upon the market are designed so that the residue may be removed and the stock of carbide replenished with the minimum escape of air into the machine or of gas into the room. A simple system of interlocking valves prevents the opening of the carbide chamber before all gas valves are closed. If operated according to instruction, no feature of the operation or care of an acetylene generator, as at present supplied, possesses any of the elements of danger. Acetylene, like any gas which will burn, will explode if mixed with air. Cubic foot for cubic foot, it covers a little wider range and is slightly more explosive than other gases. Candle-power for candle-power, other illuminating gases are from five to twelve times as explosive as is acetylene. A leak of acetylene is no more apt to occur than is a leak of any other gas under similar conditions.

An acetylene generator can, through gross ignorance or carelessness, be made to fill a basement with gas just as it can by only ordinary care be made to supply a system of burners. A

basement full of air and gas, water gas, coal gas, natural gas, or acetylene gas, is harmless unless ignited. If the basement is entered with a candle or with a lighted match, or the mixture is ignited from some external source, the results are practically identical, without regard to the nature of the gas supplying the active element.

FOURTH GENERAL MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY.

The fourth general meeting of the American Electrochemical Society was held at Niagara Falls from September 17 to 19. The number of members and guests registered was 138, a complete alphabetical list being given at the end of this report. While the attendance was less than at the two last meetings, all those who were present concurred in the sentiment that the meeting as a whole was a very enjoyable electrochemical "family affair;" there was good will and good feeling all around.

Much credit for this success is due to the efforts of the local committee. While its chairman, Mr. E. G. Acheson, was prevented by sickness from being present, the other members of the committee, and notably its indefatigable secretary, Mr. Clarence L. Collins, 2d, were restless in their endeavors to extend courtesies and to make everybody feel at home. The smoker on the evening of September 17 and the reception and dance on the evening of September 18 were well attended by the members and guests with their ladies, and were greatly enjoyed. On the afternoon of September 19 a delightful excursion was made by trolley and boat to Fort Niagara. In the afternoon of September 17 and 18 various plants were visited, which will be referred to at the end of this report. The mornings were taken up by sessions devoted to the reading and discussion of papers. The intention was to read all papers relating to electric furnaces on Thursday, all papers relating to electrolysis on Friday, and to devote the Saturday session to a general discussion of the electrolytic dissociation theory. In general, this programme was adhered to. In the following we give the papers and discussions in abstract.

Thursday Session.

At the beginning of this session the secretary, Mr. C. J. Reed, and the treasurer, Mr. Pedro G. Salom, presented their reports. The membership list has passed the 600 mark and the treasury has a surplus of $2,000. Arrangements have been completed to exchange publications with the recently founded Faraday Society of England, so that each member of the American Electrochemical Society and of the Faraday Society receives both the Transactions of the former and the organ of the latter (The Electrochemist and Metallurgist) free of charge. The foundation of local sections is approaching realization; Prof. Burgess announced that the members of Madison, Wis., are about to start a local section. Other local sections will probably be founded in the near future in New York and in Philadelphia.

Note on Some Theoretical Considerations in the Construction of Resistance Furnaces.

The first paper was presented by Mr. Francis A. J. FitzGerald, on the above subject. He divided electric-resistance furnaces into two classes: First, those furnaces in which the current passes through the whole charge, and second, those in which the current passes along a definite path or paths, thus localizing the heat. The author then discussed the furnace invented by E. G. Acheson, according to this classification.

The furnace for making graphite electrodes belongs to the first class, but is peculiar in that the heat is mainly generated outside of the articles under treatment. The electrodes to be converted into graphite are arranged in piles, and the spaces between the latter are filled with granular carbon.

Since the resistivity of the granular carbon mass is much greater than that of the electrodes, most of the heat is developed in the former. The advantage of this type of furnace is that it permits of treating a large mass of low-resistance material without using currents of excessive amperage. (See Electrochemical Industry, October, 1902, p. 53.)

As examples of the second class of furnace in which the current passes along a definite path only, the carborundum and the "white stuff" furnaces are mentioned. In the carborundum furnace the charge consisting of sand and coke in the form of powder, is placed in a box-like furnace, and through its center passes the conducting core of granular carbon or a carbon rod, connecting the terminals of the furnace. The current is confined to the core, raising it to a high temperature, and the heat generated is conducted into the surrounding mixture, converting it into carborundum. Careful temperature regulation is necessary, because if the temperature becomes too high, the carborundum is decomposed and the silicon is vaporized. (See Electrochemical Industry, October, 1902, p. 50.)

The "white stuff" furnace is of the same general form as the carborundum furnace, but has to produce only a moderately high temperature. As "white stuff" is an intermediate product in the formation of carborundum, and the temperatures between which it is formed and decomposed apparently lie near one another, the problem of its design is difficult and was solved by Acheson by the use of several cores, "definitely spaced with relation to each other at distances largely determined by the heat conductivity of the charge, the duration of the operation and the superior and inferior temperature limits of the operation." (See Electrochemical Industry, May, 1903, p. 332.)

The highest temperature is produced in the furnace for converting carbon in a bulk into graphite. The carbonaceous material, anthracite coal, coke, etc., is placed in a trough-like furnace, and through the centre of the charge is a series of carbon rods connecting the furnace terminals. Anthracite coal, the raw material usually employed, is practically a non-conductor of electricity, and first the current passes through the carbon rods, so that at the beginning of the operation the furnace belongs to the second class of resistance furnaces. But gradually the heat generated in the core converts the surrounding coal into graphite, which then becomes a conductor and heats another layer of coal, and so on till the process is complete. At the end of the operation the furnace therefore belongs to the first class of furnaces of the resistance type.

In all these furnaces the electric resistance is a variable quantity, and after a furnace is started there are no means of adjusting internal conditions so as to effect regulation in this respect. In general the resistance of the furnace is high at the beginning of a run and low at the end; therefore means of varying the voltage at the furnace terminals must be used. If the highest and lowest available voltage and the maximum available watts are given quantities, then by a simple application of Joule's law we can find the limits between which the resistance varies. The resistance may be varied by alternating

the dimensions of the core, and by judiciously choosing different forms of carbon, which have different resistances. (The case of the graphite electrode furnace is a special one, the adjusting of the resistance being obtained, to a certain extent, by the spacing between the piles of electrodes.)

The author then gives the equations for the passage of heat from a cylinder (the core of the furnace) through a heat conducting material (the charge) under certain special conditions which are only approximately fulfilled in a commercial electric resistance furnace. He then applies his formulas to the different Acheson furnaces.

With regard to the Acheson furnace for converting coal in bulk into graphite, the author shows that his formulas limit the size of the furnace in order to get high efficiency. For the carborundum furnace he arrives at the conclusion that the heat conductivity of the material around the core should be as great as possible; this can be best accomplished by having the mixture surrounding the core of high density, for then the crystal mass formed will also be dense.

While his equations involve numerous assumptions which do not represent the conditions and take no account of certain factors, the author points out that keeping the theoretical considerations in view is a great help in the building of furnaces, and prevents waste of time in experimenting with designs that cannot possibly be satisfactory.

In the discussion Dr. J. W. Richards asked what was the power factor in furnace operation; Mr. FitzGerald replied that in commercial furnaces the power factor is not unity; in fact, it was rather low in the early types of furnaces, owing to considerable self-induction due to the construction of the electric leads; but this disadvantage was partly overcome by means of interlaced bus-bars. Mr. A. H. Cowles referred to experiments made by him in 1885 in which he produced carborundum and some material apparently similar to what is now called "white stuff;" Dr. Mabery had analysed this material and believed to have found a sub-oxide of silicon. Mr. FitzGerald replied that he had made many analyses, but could not find any evidence of a sub-oxide of silicon. (See concerning this point an interesting communication by Mr. FitzGerald, published in the correspondence column of this issue.)

Mr. Carl Hering said that the formulas given in the paper would be considerably more valuable if numerical values were given for the constants entering into these formulas. Mr. FitzGerald replied that this was impossible, as his formulas were not intended to be considered as exact, but only to serve as a general guide; they should not be applied to numerical calculations.

Mr. Cowles doubted that in the carborundum furnace the current passes only through the core, and referred to the fact of a decrease of voltage at the end of a furnace run. Mr. FitzGerald replied that carborundum is practically a non-conductor of electricity, and that the crystals are so arranged as not to offer a very good continuous path for the electric current; he thinks the fact that the voltage drops at the end of a run is due to the conversion of the original carbon core into graphite, which is a much better electrical conductor. Mr. Cowles then described an experiment made by him in which during a run the carbon core (which had been suitably arranged for this purpose) was removed; the current was found to drop off one-third; he therefore concludes that hot carborundum is a conductor of electricity. Mr. FitzGerald remarked he had never read any description of this experiment; he thinks that carborundum is practically a non-conductor compared with carborundum. Prof. C. F. Burgess said that experiments in this direction had led him to the same conclusion.

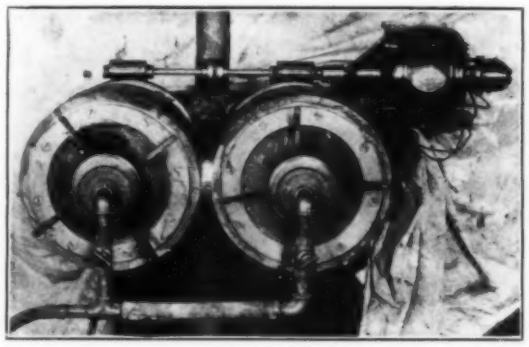
Dr. Richards asked whether any calculations of the efficiency of the furnace have been made by Mr. FitzGerald. The latter assured that he had commenced such calculations, but on account of the many doubtful "constants" which enter into the problem, he gave it up as a bad job.

Advance in Electrometallurgy of Iron Production.

A short paper with this title was presented by Mr. Marcus Ruthenburg, who referred to his paper of last year (Electrochemical Industry, November, 1902, p. 84), and reported advances made in his process since that time. He agrees that the blast furnace is a highly economical device for accomplishing its end, and will continue to be so until methods be found that will perform its functions for less money.

For certain cases, however, the blast furnace is unsuitable. For instance, given a magnetic ore-carrying gangue, with sulphur and phosphorous in prohibitive quantity for making good steel economically, such ores find no market tributary to the blast furnace. On the other hand, such ores may be crushed, magnetically concentrated, electrically smelted and produce the best of steel at a price which can compete with an ideally situated blast furnace. For this purpose the Ruthenburg process is intended to be used.

The crushed ore, having been magnetically concentrated, drops into a magnetic zone between two revolving cylinders, where it forms a bridge, due to the action of the magnetic field, and is electrically melted; it then becomes unmagnetic and drops down into the soaking pit. New material forms then a bridge and so on. (For further details see Electrochemical Industry, February, 1903, p. 202, also the description of the Ruthenburg plant at the end of this report.) The



RUTHENBURG FURNACE, FRONT VIEW,
Showing the Water-Cooled Magnetic Poles and the Bridge of Ore, Being Smelted.

action of the electric current is only to melt the dusty particles, to agglomerate them into coherent masses without binder or flux, and to convey a sufficient quantity of heat to the ore in the soaking pit. The reduction takes place in the soaking pit through which heated hydrocarbon gases or CO are passed.

Three problems were to be solved in the evolution of this process; first, the electric power required to agglomerate and sufficiently heat the material for subsequent reduction; second, the regulation of the size of the agglomerated particles; and third, the amount of reduction of the agglomerated material. The status of the solution of these three problems is given by Mr. Ruthenburg as follows:

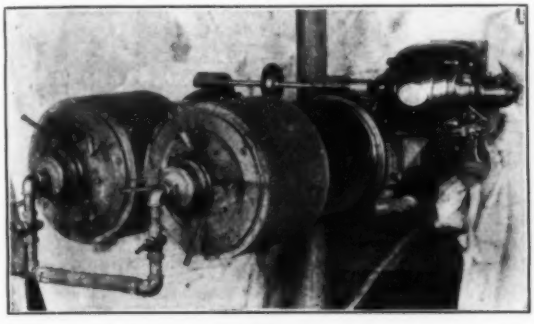
First, a ton of ore is being agglomerated with an expenditure of about 250 kw.-hours (against 500 kw.-hours last year, this improvement being due to the use of the new apparatus). Second, the size of the product is under perfect control. Third, the reduction is being made absolute.

In the discussion which followed, Mr. C. J. Reed asked as to the efficiency of the process. Mr. Ruthenburg replied he had made no such calculations; all he does as a practical engineer is to weigh his ore, to analyse it before and after treatment, and to measure the consumption of energy by means of a recording wattmeter. Mr. Cowles, however, gave figures of the thermochemistry of the process.

Dr. G. P. Scholl asked as to the analysis of the material; Mr. Ruthenburg replied that phosphorus is removed by the preliminary magnetic separation; if, however, any phosphorus should get into the electric furnace, it would not be eliminated; on the other hand, he is convinced that sulphur is absolutely eliminated, due to the reaction between Fe_3O_4 and FeS_2 at the high temperature (about 1200°) in the melting zone of the electric furnace.

Mr. Beckett questioned the possibility of a complete removal of sulphur; he had made a series of experiments in the same line, but was unable to get iron free from sulphur; he also referred to the impossibility to solve the analogous problem to get metallic nickel by the reaction of nickel oxide and sulphuric sulphide. Mr. Ruthenburg replied that in his experiments he had found the amount of sulphur in the final product to be very small. Dr. Richards said that magnetic ore is in itself low in sulphur.

Mr. Cowles pointed out that the only material which drops into the soaking pit is iron oxide after having been fused; when it is accumulated in the pit, it represents a heated mass in a retort, through which the heated hydrocarbon gases are passed to produce the reduction; the material in the soaking pit is at the right temperature required for reduction. Mr. Ruthenburg called attention to the fact that iron is peculiar, in so far as the reduction of iron oxide by CO takes place at a comparatively low temperature, somewhat above that of boiling water; this is the temperature in his soaking pit. He considers



SIDE VIEW OF RUTHENBURG FURNACE.
The Small Motor at the Right Hand is Used for Revolving the Two Rolls in the Front.

this as one of the principal points in which he saves energy, compared with other electric steel processes, because, in his process, the heat and current losses due to maintaining a molten mass are lacking.

President Richards, in concluding the discussion, referred in some complimentary words to Mr. Ruthenburg as one of the successful pioneers in a new field of electrometallurgy in this country. He expressed his belief that when electric steel processes will once become industrial processes, they will become the largest electrochemical industry.

AN ELECTROLYTIC PROCESS OF REMOVING BRASS FROM STEEL.

Prof. CHARLES F. BURGESS presented a paper on "a practical utilization of the passive state of iron." It has long been that iron or steel, when used as anode in a solution of sodium nitrate or of various other soluble nitrates, soon assume what is called the passive state, i. e., they are no longer attacked by the anode products, and behave just like a platinum anode, oxygen gas being liberated. The passive state thus produced is probably the same condition which iron assumes when immersed in concentrated nitric acid. The author describes a process in which this passive state is made use of in an industrial way.

An improvement in the method of brazing employed extensively in the manufacture of bicycles consists in dipping bodily a portion of the frame to be brazed into a bath of melted spelter, which is covered by a suitable flux. By this operation not only is the brazing effected within the joints, but a thin layer of brass adheres to the outer walls of the tubing, so that it becomes necessary to remove this layer in preparing the frames for receiving a coating of enamel. To effect this by filing, entails a large amount of labor and frequently the thin tubing is damaged, as some of the iron is removed as well as the brass.

In experiments made by the author, it was tried to find an electrolytic process by which the brass could be removed electrolytically from the iron; but with a great many electrolytes, tried at first, the iron tended to corrode much more readily than did the copper which enters into the constitution of the brazing smelter. The reason is that iron has a position considerably above copper in the electrochemical series of elements, and where two different metals are in contact, the natural tendency is for the more electropositive one to go into solution with the greater ease.

The solution of the problem was that by using a sodium nitrate solution, iron is made to assume the passive state, its position in the electrochemical series of elements is changed, it becomes more electronegative than copper. With such a solution it was found that the brass could be completely removed and the iron left intact. This method of electrolytic stripping was installed and operated with success in various factories, and is now an important adjunct to the dip-brazing method. This same electrolytic stripping process may be applied equally well in removing silver, lead, tin and other metals more electronegative than iron from an iron surface. Nickel cannot be removed in this way, however, since nickel, as well as iron, assumes the electronegative or passive state.

The author then gave some measurements of the single potential of iron in a normal sodium nitrate solution, determined against the Ostwald calomel standard electrode, the potential of which was taken as —0.56 volt. The single potential of iron in $NaNO_3$, before any current is passed through the iron as anode, is in the neighborhood of +0.2 volt; in other words, a potential is set up towards the solution in the same direction, but of less magnitude than would be produced by zinc. By causing the current to pass from the iron as anode, however, this potential quickly becomes negative, and increases rapidly in negative value, until a potential as high as —2.0 volts can be obtained under certain condition. A sudden and considerable increase of the potential takes place at the moment when the iron assumes the passive state. This occurs with greater rapidity, and at a much lower current density, if some $NaNO_2$ is added to the $NaNO_3$ solution. This fact explains why the iron does not assume the passive condition when used in sodium nitrate solution freshly prepared, but only after the current has passed for some time; at the cathode sodium is liberated which unites with the water to form sodiumhydroxide, and the hydrogen thereby set free reduces the sodium nitrate to nitrite.

On the other hand, copper, when used as anode in sodium nitrate, does not change its potential in anywhere near the same degree, so that the iron may readily be made much more electronegative than copper. If an iron and brass plate are exposed simultaneously to the solution as anodes, each plate being connected through an ammeter to the same source of current, on closing the circuit almost all of the current passes through the iron anode, but after operating for a few seconds the iron becomes passive, after which the brass takes all of the current. By using very high current densities, however, the iron may begin to conduct a small portion of the current, thus causing a liberation of oxygen on its surface.

In the discussion Mr. C. J. Reed referred to a case in which lead is changed to lead peroxide and then acts like platinum, evolving oxygen at its surface, and asked whether Prof. Burgess would call this the "passive state of lead." Prof. Burgess replied that the behavior is quite similar in both cases, but he would apparently not commit himself to a direct statement

that it is a coating of iron oxide which produces the passive state of iron, as this is a disputed question.

Friday's Session.

An Experiment on the Electrolytic Determination of the Basicity of Acids.

A paper on this subject was presented by Mr. Ivar Juel Moltkehansen. He referred to the fact that measurements of the electrolytic conductivity in connection with Ostwald's dilution law have been successfully used to reach a decision in cases in which complex acids of doubtful basicity were in question. He has used this method in the study of the constitution of the metaphosphoric acids.

The question of the constitution of the different metaphosphoric acids can only be solved by analysis of their double salts, as the determination of their vapor density is not practicable, owing to the decomposition of the metaphosphate vapors, even at a low pressure. The metaphosphates are dissociated in a water solution, and their molecular weight cannot, for this reason, be determined by the methods of lowering of the freezing point or the increase of the boiling point. They are not soluble in solvents containing no hydroxyl, such as benzol or chloroform. A decision as to the constitution of the water—soluble metaphosphates is, however, possible according to their conductivity for the electric current.

The author investigated Glatzel's and Fleitmann's dimetaphosphoric ammonium, by examining its equivalent conductivity in suitable dilutions and applying the formula given by Ostwald. The measurements were made by the method of Kohlrausch with the Wheatstone bridge connections and telephone. His measurements show the acid to be dimetaphosphoric acid in the ammonium salt, with two molecules of water of crystallization. On the other hand, Warschauer has arrived by similar measurements at the conclusion that Fleitmann's dimetaphosphoric acid does not exist, but that the acid described as such by Fleitmann and Glatzel is tetrametaphosphoric acid. Further investigations are necessary to explain this discrepancy.

Electrometallurgy of Gold.

A paper on this subject was presented by Dr. W. H. Walker. The electrometallurgy of gold is based on the facts that the electric current may be used to advantage both for dissolving metallic gold in a cyanide solution in form of the double salt $AuKCy_2$, and for depositing it from such a solution. The effect of the current in the process of dissolving appears to be that it supplies oxygen, for it has long been known that the process of dissolving Au in an aqueous solution of K Cy requires the presence of oxygen. On the other hand laboratory experiments have shown that in a $KAuCy_2$ solution the cation is K and the anion is $AuCy_2$; this is of great importance for the process of precipitating the gold from the solution. What is primarily precipitated, is the cation K, which then acts on the $KAuCy_2$ solution with the resulting secondary precipitation of gold. The gold is, therefore, contained in the anions which travel away from the cathode so that the current tends to impoverish the solution in gold near the cathode. On the other hand, it is just at the cathode where the gold is wanted, in order to enable the secondary reaction between the primarily deposited potassium and the $KAuCy_2$ to take place. This shows the importance of stirring and agitation for the process of precipitation, and it also explains why the efficiency will be small.

The author then gave a review of the electrochemical gold processes and divided them into two classes. The first class comprises those processes in which the solution and precipitation do not take place simultaneously. The Siemens & Halske process belongs to this class; it is used on a large scale in South Africa. The ore is first leached out in the leaching plant, and is then supplied to the precipitating tanks; the older and newer arrangements of the electrodes were described. The main advantage claimed for the electrochemical precipitation of gold over the chemical method by means of zinc shavings, is that the former requires less concentrated solutions and the consumption of cyanide is smaller.

The second class of processes comprises those in which the solution and precipitation takes place simultaneously. The author described and discussed the following three processes: Pélatan-Clerici, Riecken, and "Aurex-Sluice." The reason why these processes have failed on an industrial scale seems to be that great quantities of ore are required to recover a small quantity of gold, and that these great quantities of ore must be continually moved.

The author finally gave an account of some experiments made by him on the cathodic reduction of gold telluride. The results prove that the electrolytic processes working on this class of ore recover their values in greater part by cathodic reduction than they do by first dissolving the mineral in the anode liquor with the subsequent precipitation of the gold on the cathode. Good contact with the cathode is therefore the essential requirement, and this was not appreciated by the first experimenters. This is an example showing why some processes may be successful in the laboratory and later fail on a commercial scale.

In the discussion of the paper Dr. Bancroft referred to a published statement that the Siemens & Halske people in South Africa do not use the Siemens & Halske process, but have bought the Andreoli patents and work under the same; Andreoli uses lead peroxide anodes and iron or aluminium cathodes. Dr. Richards referred to experiments made by him to determine the efficiency of the Siemens & Halske process on a laboratory scale; the best results gave an efficiency as low as ¼ per cent; he pointed out, however, that in the economical production of gold the cost of power for electrolysis, and, therefore, the efficiency of the electrolytic process does not cut any figure whatever.

Electrolytic Copper Refining.

Prof. Wilder D. Bancroft presented a paper in which he gave an account of a series of experiments made under his direction in Cornell University by Messrs. Schwab and Baum. The first object of the investigation was to determine the most economical current density and temperature for the process of copper refining. With increasing current density the cost of power necessary for precipitating a given weight of copper increases, while the interest charge on the copper in the tank decreases. Good adherent copper can be obtained at almost any current density, provided the rate of circulation be sufficient. With rising temperature the cost of power decreases, while the cost of heating the tanks increases.

To strike a balance between these conflicting factors, the relation between voltage, current density and temperature for pure copper plates, set a definite distance apart, was determined in four solutions of compositions used in practice. By expressing the voltages in terms of the voltage at 20°, the effect of the distance between the plates was eliminated, and the percentage variations hold for any set of plates in the same solutions.

Data were also obtained showing the relations between current efficiency, current density and temperature for pure copper plates in the same four solutions. Finally the variation of the cost with varying conditions of temperature and current density were determined for the case of all power costing at the rate of $20 per horse-power-year, and also for the case in which steam heating costs only one-thirtieth of electrical heating.

The object of the first test were to determine the variation of voltage with variation of temperature current density and solution. The following four solutions were used: first, 16 per cent $CuSO_4.5H_2O$ and 9 per cent H_2SO_4 (commercial solution used in refineries with multiple system); second, the same with a small addition of NaCl (1÷2,000,000 of solution);

third, 16 per cent $CuSO_4$, $5H_2O$, and 6 per cent H_2SO_4 (commercial solution used in refineries with the series system); fourth, the same with a small addition of NaCl. The experiments were made on a small experimental scale, beakers being used, instead of tanks.

The results were given by Dr. Bancroft in a series of tables for temperatures between 20° and 90° C., and current densities between 1 and 4 amperes per square decimeter. The voltage required to obtain a given current density is materially less with the 9 per cent acid solution than with the 6 per cent acid solution. The addition of sodium chloride to the solution increases the voltage at the lower temperatures, while the effect is scarcely noticeable at the higher temperatures.

The object of a second test was to determine the variations of the ampere-hour efficiency when operating with the same four different electrolytic solutions at varying temperatures and different current densities. It was found that the ampere-hour efficiencies for temperatures below 70° C. fall off but very little, and are practically 100 per cent. Even at a temperature of 90° C. and the nigh current density of 4 amperes per square decimeter the efficiency runs as high as 98 per cent and 99 per cent for the 9 per cent and 6 per cent solutions, respectively, while a current density of 1 ampere per square decimeter gives an efficiency of 90 per cent and 91 per cent. Between 50° and 70° the efficiency in some cases runs a trifle above 100 per cent, due to the formation of cuprous sulphate in small quantities in the electrolyte. (Foerster and Seidel found that the current efficiency drops off rapidly above 50° C., but they used very low current densities, 1 ampere per square decimeter being their highest density.)

The deterioration of solution is proportional to the ratio of anode loss to cathode gain, since pure copper plates were used and there was a sediment or copper scrap on the bottom of the beakers. The solution deteriorates more rapidly at the higher temperatures and at the lower current densities. This deterioration of solution probably more than offsets the advantage of decrease in voltage which the higher temperatures give, but only when operating at the lower current densities. The ratio of anode loss to cathode gain, when operating at 70° C. and 4 amperes per square decimeter, is hardly any higher than this ratio for operating temperatures between 20° and 50°.

The author gives in a series of tables the watt-hours per gram of copper for the different solutions under different conditions, also the ratio of the watt-hours at higher temperatures to those at 20°, and the ratio of the corresponding voltages. As an example we give the results for the 9 per cent acid solution without NaCl, for current densities of 3 and 4 amperes per square decimeter:

	Ratio of voltage to that at 20°.	Ratio of watt-hours to those at 20°.
20° C. 3 amp. per sq. dm	1.000	1.000
50° C. 3 " "	0.600	0.600
70° C. 3 " "	0.441	0.440
90° C. 3 " "	0.347	0.354
20° C. 4 " "	1.000	1.000
50° C. 4 " "	0.605	0.605
70° C. 4 " "	0.454	0.454
90° C. 4 " "	0.362	0.368

In a special test with solutions containing iron, no falling off in the current efficiency could be found.

An important part of the investigation was the radiation run, made to form some idea of the relative costs of operating at various temperatures, with covered and uncovered tanks. The temperature of the electrolyte in a covered tank decreased from 96.1° to 44° C. in 123 minutes; in the same tank, uncovered, from 94.5° to 44.7° in 60 minutes. The power in watts required to overcome the radiation of heat and keep the temperature unchanged, is given in the following table:

	90	80	70	60	50 degs. C.
Covered tank ..	44.0	36.6	28.8	21.7	14.5 watts
Uncovered tank.	145.0	90.4	50.6	34.4	20.6 watts

These figures refer to the small tanks used in the experiments. To get the watts for commercial tanks of 9 x 2 x 2½ feet, as used in the Baltimore refinery, the figures in the table are to be multiplied by 100.

In a further test an attempt was made to duplicate commercial conditions in the precipitation of electrolytic copper. Finally the data obtained in all of these tests were used by Dr. Bancroft to calculate the cost of refining. The basis of this calculation was: Dimensions of tank, 2 x 2½ x 9 feet; one tank containing 130 electrodes of two plates each; weight of copper per tank = 5,700 pounds; value of copper per tank = $800, cost of power = $20 per horse-power-year; plant temperature = 20° C. The calculation is on the basis that the heating of the electrolyte is done by means of the electric current and that the ampere-hour efficiency is 100 per cent.

The following three items of cost were taken into consideration: Cost of kilowatt-hours required to precipitate one tank of copper; cost of heat required to keep the temperature of the electrolyte constant; interest on the copper in one tank at 6 per cent. The sum of these three items is called "total cost" and is given in dollars in the following table, which is only an extract from that given in Dr. Bancroft's paper.

COST PER TANK OF COPPER.

Amperes per sq. dm.	At 50° C.	At 70° C.	At 90° C.
2.0	$2.70	$3.87	$5.09
3.0	2.58	2.57	3.39
4.0	2.72	2.33	2.54

As stated before, these figures give the cost per tank of copper. The following table gives the corresponding figures per ton of copper:

COST PER TON OF COPPER.

Amperes per sq. dm.	At 50° C.	At 70° C.	At 90° C.
2.0	$0.95	$1.36	$1.79
3.0	0.91	0.90	1.19
4.0	0.95	0.82	0.89

While these figures are based on experiments with the series system, it is probable that the conclusions to be drawn would apply equally well to the multiple system. The kilowatt-hours per kilogram of copper will be larger in a multiple tank, owing to the greater distance between plates. The radiation losses are probably also greater, owing to the tanks being relatively wider. Otherwise there is little difference, since the extra interest charge in the multiple system, owing to the use of thick anodes, is offset by the possibility of removing the cathodes before the end of the run, which cannot be done in the series system.

As in practice the solutions are heated by steam coils, and as this costs less than electric heating, the following table gives the results calculated on the basis of electric power at $20 per horse-power-year, and steam heating at one-thirtieth the price of electric heating:

COST PER TON OF COPPER.

Amperes per sq. dm.	At 50° C.	At 70° C.	At 90° C.
2	$0.91	$0.83	$0.80
3	0.91	0.78	0.72
4	0.95	0.82	0.89

The commercial cost per ton of copper will be between the figures given in the last two tables, which are, therefore, to be considered as limits. These figures of cost comprise only the three items stated above. They do not include the cost of labor, and are based on the assumption of 100 per cent ampere-hour efficiency. Since the number of men employed does not vary with the current density, the cost of labor per ton of copper will be less, the higher the current density. The correction for the actual current efficiency is easy to apply when one has the data, and will not affect the general results, because the current efficiency is practically independent of the temperature and current density at temperatures below 90°

and within the range of current density considered. The question of the deterioration of the electrolyte need not be considered, because the amount of deterioration is also practically independent of the temperature and current density at temperatures below 90°.

To apply these results to the commercial problem of copper refining, two sets of curves were plotted, one showing the relation between the cost of precipitating a ton of copper and the operating temperature, the second set showing the relation between the cost of precipitating a ton of copper and the operating current density. From these curves the conclusion was drawn that the results at 70° C. seem the most satisfactory with a current density of 3.5 and 3.75 amperes per square decimeter. Under these conditions no extra power would be required to heat the solution. Operating at this current density *with covered tanks*, the current alone would be sufficient to heat the electrolyte to over 80° C. In order to secure good circulation, essential for a good deposit with high current densities, the method of pumping could be retained. If the gutters leading to and from the pump were properly insulated, the solution would not drop below 70° C. before returning to the tanks. Moreover, running at this high current density, there would be a considerable saving in the first cost of the plant, inasmuch as fewer tanks are needed for the precipitation of a given amount of copper in a given time.

The lower the cost of heating, the greater the advantage of a high temperature. Lowering the rate of interest decreases the advantage of a high current density. With covered tanks, it will be possible for men to work in the tank room even with the electrolyte at 70°.

If the cost of working under so-called standard conditions for open tanks, i. e., a current density of 14 amperes per square foot, and a temperature of 50°, is compared with the cost of working with covered tanks at 70° and a current density of 3.5 amperes per square decimeter (31.5 amperes per square foot), the saving by the latter method will be very close to $1.00 per ton of refined copper when all power is figured at $20 per horse-power-year.

Therefore, in order to operate a plant most economically, Dr. Bancroft concludes, copper should be refined electrolytically under these conditions: Covered tanks; current density 3.5 amperes per square decimeter; temperature 70° C.

In the discussion which followed Dr. Bancroft's paper, Dr. Richards read three communicated discussions by Mr. Benjamin Magnus, superintendent of the Anaconda refinery, Mr. Lawrence Addicks, electrochemist of the Raritan Copper Works, and Prof. T. R. Rosebrugh.

Mr. Benjamin Magnus stated his experience had been that the ampere-hour efficiency depends entirely on mechanical conditions. If a tank is kept free of most local short circuits, one may very easily attain a desirable maximum ampere-hour efficiency in practical refining. By "desirable maximum efficiency" he means an efficiency which can be obtained by an expenditure of labor which costs less than the gain to be gotten by a higher efficiency. Where the general efficiency is 95 per cent he had succeeded in getting it up to 97.5 per cent, but the extra labor was not saved by the extra saving in power.

Concerning the statement of Dr. Bancroft that the solution deteriorates more rapidly at the higher temperatures, and at the lower current densities, Mr. Magnus stated he had found this true for high temperatures, but not for low current densities. At the Anaconda plant, where a low current density is used, they have been able to use the same electrolyte continuously for many years; but at other plants, where the current density is 60 per cent higher than at Anaconda, they found it necessary to renew some part of their electrolyte frequently. At low current densities the oxidation of impurities occurs quite freely, thus keeping the electrolyte from becoming fouled with impurities.

Mr. Magnus then criticised Dr. Bancroft's statement that since the number of men employed does not vary with the current density, the cost of labor per ton of copper will be less the higher the current density. In actual practice this is not the case. High current densities cut down the interest on copper tied up and the interest on investment for plant, etc. But, as a matter of fact, the plants having high current densities usually have higher labor costs per ton of copper produced than plants using low current densities. Mr. Magnus referred to two well-known plants which use respectively 10.5 and 40.0 amperes per square foot, the one with the higher current density having a labor cost 40 per cent greater than the plant using the lower current density. Concerning the proposal of covered tanks Mr. Magnus said that only a casual inspection of a tank room in any practical plant would soon convince a visitor of the objection to covering tanks.

Mr. Magnus finally discussed, by way of demonstration, the conditions at the Anaconda refinery. The current density is 10.5 amperes per square foot, the temperature of the electrolyte is 100° F. and the circulation of the electrolyte is 3 gallons per minute. Under these conditions the chemical action in the tank is 1 per cent greater than the electrolytic action, and the voltage per tank is 0.23 volt. In order to keep the solution constant day by day, the extra copper taken up by the solution, due to the 1 per cent greater chemical action, is taken out by means of a tank which has insoluble anodes. The cost of operating this tank is at least eight times the cost of operating a regular depositing tank, the voltage being 2 in the former. Most electrolytic plants use exhaust steam for heating the electrolyte, but even if they used live steam, which costs $80 per horse-power-year, the cost of heating the electrolyte per ton of copper produced would only be from 16 to 35 cents; and if they raised the temperature of their solution to 70° C. and raised the current density to 31.5 amperes, the excess chemical action would be so great that to free the electrolyte from copper, by means of tanks having insoluble anodes, would cost so much that the saving of power due to warmer solutions would be more than offset.

Mr. Lawrence Addicks said that electrolytic refining from a stanpoint of economy consists of a very nice balance of a number of conditions, and that while Dr. Bancroft has considered some he has in turn overlooked others which cause him to arrive at what, in the mind of Mr. Addicks, are erroneous conclusions. While it is true that good adherent copper can be obtained at almost any current density, provided the rate of circulation be sufficient, yet we are limited in circulation to a very small rate; otherwise we have a turbid solution and a cathode which is not only impure, but carries a prohibitive amount of silver. A system where a torrent of circulation carries all slimes rapidly out of the tank to be settled or filtered out in the dump might avoid this, but there is no such system in use, and the conclusions reached in the paper are applied to existing plants. Insufficient circulation at once means poor deposition and necessitates frequent renewal of the cathode sheets to maintain the current efficiency and entails a corresponding increase in labor lost. Take the Anaconda and Great Falls plants for example; the former, with a density of 11 amperes per square foot, draws copper every 35 days; the latter, with 40 amperes, every two days. Less than four times the density and but a seventeenth of the age. While Dr. Bancroft did not claim to consider labor cost, yet Mr. Addicks thought we must consider labor cost to make any such sweeping statements as those at the end of the paper.

Mr. Addicks said that Bancroft's work on temperature coefficients was more complete than any he had seen elsewhere, and very interesting, but that the idea of covered tanks would be greeted with much hesitation by most refiners. It is hard enough to get thorough inspection on with an open tank, let alone a closed one. With very high temperatures they would undoubtedly be warranted, as otherwise the vapor in the air would make work unbearable. Their application to a series tank would be much simpler than to a multiple one with its external connections. Mr. Addicks expressed the opinion that

if interest and depreciation on the plant were considered in Bancroft's cost tables, the changes would revolutionize them.

Mr. Addicks concluded that current density and temperature of electrolyte bear vital relations to the cost of refining; while Dr. Bancroft has furnished some valuable data, and for some refinery his conslusions are true, yet against their application to every plant that can obtain power for $20 a horse-power-year, he would protest.

Prof. T. R. Rosebrugh criticised the cost of $20 per electric horse-power-year, and the assumption that the cost of steam heating is one-thirtieth of electric heating.

Mr. Woolsey McA. Johnson referred to some similar experiments made by him some time ago on nickel refining; he had also plotted similar curves, but he emphasized that the results of such curves must be translated freely into practice. He criticised a statement of Dr. Bancroft concerning the observation that during the last commercial test the voltage across the terminals of the tank rose from 1.75 volts at the beginning of the run, to 2.10 volts three and a half days later, which was attributed by Dr. Bancroft to the deterioration of the solution, i. e., to the neutralization of the acid. Mr. Johnson thought there were two other reasons for this rise of voltage, the increased resistance of the slimes and the concentration changes in the slimes.

Dr. Bancroft, in his reply, first referred to the criticism of Prof. Rosebrugh and stated that his assumption of $20 per electric horse-power-year was simply taken as a standard; if at any other place the cost is different, then one can easily make the calculation. His assumption concerning steam heating is to be considered only as a limit. Concerning the rise of voltage, he said that Mr. Johnson's criticism was disproved by the experiment, because the voltage assumed again its original value when the electrolyte was restored to its original condition; of course, in the nickel refining process from which Mr. Johnson had derived his argument, the conditions may be different. Replying to Mr. Magnus and Mr. Addicks he said that his experiments showed no greater deterioration to take place at 70° C. than at lower temperatures. He expressed his belief that the objections raised against covered tanks were greatly overstated; it is not difficult to arrange the covers so that they may be easily lifted, and if this is done, the only difference with present practice will be the slight extra time necessary to swing or lift the covers. On the other hand every refiner should carefully consider that covered tanks may mean a saving of 30 per cent of power, even under the present conditions of current density and temperature.

Concerning the criticisms that in his cost tables he had overlooked important factors, Dr. Bancroft said that he had clearly stated all factors which he had considered and those which not; on the basis of his experimental results every refiner is now enabled to make the calculation of the most economical current density and temperature for his own refinery, using his own figures.

Corrosion of the Nickel Anode in Nickel Plating.

A paper on this subject was presented by Prof. Oliver W. Brown. In the absence of the author it was read by Mr. W. McA. Johnson. The author pointed out that a plating bath must be considered as a whole; while a good cathodic deposit is the goal to strive at, it is necessary to also consider carefully the condition of the anode. To get high efficiency it is necessary that the anode shall corrode at the same rate as the nickel is deposited on the cathode.

If this would be the case, the e. m. f. at the terminals of the cell would be only necessary to overcome the resistance. In reality there is, however, a counter e. m. f. of polarization at the anode. To study this problem in detail, the author measured the single anodic potential (against an Ostwald calomel standard electrode, the potential of which is taken as —0.56 volt) and used various kinds of nickel for the anode. Some of the most important results are given in the adjoining table, 0.45 ampere hour being used in all cases.

Nickel Anode	Amperes per Square Foot		Discharge Potential in Volts		Current Efficiency	
	Anode	Cathode	Anode	Cathode	Corrosion of Anode	Dep. of Nickel on Cathode
Cast, surface ground smooth	4.12	2.21	—1.834	+0.308	46.29%	75.42%
Cast, surface roughened in acid	4.12	2.21	—0.44	0.252	91.32	92.08
Rolled, pure	4.42	4.42	—1.889	0.145	8.47	63.27
Electrolytic	4.42	4.42	—1.883	0.143	12.65	61.61

The results show that electrolytic nickel anodes corrode very poorly, as compared with cast anodes; also that pure rolled anodes are no better than the electrolytic. The different efficiencies obtained with cast anodes of smooth and rough surface are of interest. The cathode efficiency is affected to a marked degree by the anode efficiency. From further experiments it seems that the highest cathode efficiency is obtained when the cathode discharge potential lies between +0.22 and +0.29 volt. The anode voltage increases very fast as the anode efficiency begins to diminish. It appears that an efficiency of corrosion exceeding 90 per cent cannot be expected if the anode voltage is allowed to get much above —0.46 volt.

The author concludes that the satisfactory operation of a nickel-plating solution depends to a large extent on the character of the anode employed. This is a fact which has been recognized by platers as a result of practical operation. It might be a natural supposition that the best results should be expected with the purest anode material, but this apparently is not the case. It appears that the presence of copper is advantageous to a certain extent, and it is quite likely that certain other impurities which are usually present in cast nickel may be equally advantageous. It has been shown that rolled nickel or electrolytic nickel are decidedly unsatisfactory for anode service, and the reason that the cast nickel shows a superiority may be due to the impurities or to a different physical structure, which gives rise to a great porosity and roughness of the surface, and thereby a greater actual surface area.

In electroplating operations the cathode has naturally been the point to which most attention has been given in the production of certain qualities of deposit, but a study of the conditions at the anode is equally important, for if the corrosion at that point is satisfactory the cathode will largely take care of itself. The lack of efficient corrosion at the anode results in an excess of acid being formed, which, diffusing to the cathode, causes a lower efficiency at that point as well. A change of efficiency at the anode is in a very short time made apparent by a similar change at the cathode. In instructions which have been published from time to time for operating nickel-plating tanks, the voltage which is necessary for plating is referred to in an indefinite way. This is probably due to the fact that the e. m. f. required under different conditions is of a considerably different value, so that no definite rules can be laid down. The electroplater can obtain an efficiency of 90 per cent or more if cast anodes are used, with an anode density of about 5 amperes per square foot. The best method of obtaining a check on his efficiency is by the determination of the anode discharge potential. This should not be allowed to reach a greater value than —0.45 volt (measured by the Ostwald standard electrode).

The Ostwald standard electrode might be considered too much of a scientific piece of apparatus. The measurement of the polarization of the cell, while much simpler, is not as definite in its indications as the measurement of the individual potential of each anode and cathode separately.

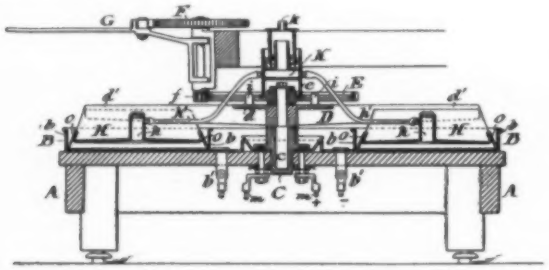
Nevertheless, the simple measurement by means of a voltmeter, of the counter e. m. f. of polarization in the cell, will serve as a general means for determining whether the cell is operating properly. When the polarization goes much above 0.75 volt, the assumption is justified that the anode is not corroding properly, and on the other hand, if the polari-

zation is below 0.70 volt the efficiency at the anode is as high as can be obtained. The means for measuring this polarization is at the disposal of most electroplaters, the method consisting in connecting a voltmeter to the anode and cathode terminals while the current is flowing, and then suddenly interrupting the current and noting the pressure between the electrodes immediately after. This reading should be taken as quickly as possible, as the polarization decreases rapidly after interrupting the current.

In the discussion which followed, Mr. Woolsey McA. Johnson spoke highly of the paper and recommended the study of the anodic and cathodic potentials against a standard electrode as one of the best means of ascertaining what is going on in an electrolytic cell. He thought that the method might be too complicated and expensive for the average electroplater, a good potentiometer costing about $150. But the simple measurement of the total polarization, recommended by Brown at the end of his paper, might be a good substitute, and would require no special instruments nor scientfic training. He criticised Brown's paper in so far as not enough analyses had been made.

Prof. Burgess said that the Ostwald standard electrode is a very handy instrument; it is simply constructed, and he has found it to be of the greatest use in his laboratory; the potentiometer arrangement used by Brown was a home-made affair, and costs less than one-tenth the amount mentioned by Mr. Johnson.

Dr. J. W. Richards referred to the statement in Brown's paper that some impurities in the anode seem to have a good effect on the corrosion of the nickel; he thought this might be explained by assuming local action, the pure nickel and the impurities, in contact with each other, acting as anode and cathode respectively in a short-circuited cell. Dr. R. Gahl objected to this explanation on account of the overvoltage on nickel; this remark precipitated some discussion between Messrs. Reed, Richards and Gahl on the subject of overvoltage.



SALOM ELECTROLYTIC CELL.

A New Type of Electrolytic Cell.

A paper on this subject was presented by Mr. Pedro G. Salom. His new type of cell, while applicable to other electrolytic processes, is mainly intended to be used in connection with his electrolytic process of reducing galena to spongy lead; this is done by using the galena as cathode in an electrolyte of sulphuric acid, the sulphur of the galena going off as hydrogen sulphide. (See Electrochemical Industry, September, 1902, p. 18.)

His older type of cell had two serious disadvantages: First, the operation was not continuous; second, the reduction of galena to lead was not complete. These disadvantages have now been overcome; by the use of his new cell, the process has been made continuous, while the reduction is now nearly complete (about 98 per cent). The incomplete reduction in his former apparatus was due to the use of too thick a layer of galena; by diminishing the thickness of the layer of ore, he found the reduction to become more and more complete; but for very thin layers of ore the old type of cell was not suitable. At the same time he found that a much higher current density than formerly used now becomes thoroughly feasible. He now uses a current density of 30 amperes per square foot and thinks he may go up to 60 amperes. This reduces the time required for reduction enormously (about 1½ hours now, against five days before).

His new cell is shown in the adjoining diagram, A is a wooden table on which the cell is mounted. The cell consists of an annular body B, of a trough-shaped cross-section, with inner and outer peripheral walls bb. It is composed of antimonial lead and is made a cathode by means of the connection b'b'. The anode consists of a series of segmental plates H, supported by the spider frame D, and bridging the spaces between seven of the eight arms of the spider frame D, the space between the seventh and eighth arm being left open. Current connection to the anode is made through the socket C and upright post c. Either the anode or the cathode is rotated by mechanical means, and the reduction of the galena is completed when the revolving electrode has made a complete revolution, i. e., in about 1½ hours under the present conditions.

In order to prevent the escape of gases anywhere else but through the pipe h, both of the peripheral surfaces of the ring formed by the anode segments are provided with rubber petticoats *o o*, which sweep against opposite walls of the cell B. A box which is filled with the material to be acted upon is arranged in the open space between the seventh and eighth arms of the spider frame, and is provided with a feeding slot, by which a continuous stream of material, the thickness of which can be varied, is fed to the bottom of the cell. A scraper-plate is also arranged which, as the annular anode rotates, sweeps the spongy mass out of the apparatus.

Formerly the handling and removing the electrodes had dangerous and injurious effects upon the workmen. This has now been completely overcome. (See also the notes on the present plant of the Electrolytic Lead Reduction Company at the end of this report.)

The paper was not discussed.

Electrolysis of Sodium Hydroxide by Alternating Current.

A paper on this subject was presented by Mr. Carl Hambuechen, and in absence of the author it was read by Prof. C. F. Burgess. As is well known, the author and Prof. Burgess have developed jointly an alternating current rectifier, based on the property of the aluminium electrode, to act as an electrolytic "valve", allowing the current to pass in one direction, but not in the other direction; their rectifier consists of an aluminium and an iron electrode in fused sodium nitrate as electrolyte. In the present paper the author describes the application of this property of aluminium to the construction of a cell which acts both as a rectifier and an electrolyzing cell, for the production of metallic sodium from fused sodium hydroxide (which does not attack seriously aluminium while aluminium is actively corroded by an aqueous solution of sodium hydroxide.) The e. m. f. required for this electrolysis is 4 volts, while the aluminium retains its property to act as electrolytic valve in this electrolyte up to 40 volts. The arrangement of the apparatus is as follows:

In an aluminium vessel sodium hydroxide is fused; in it is placed an aluminium electrode and, surrounding it, an iron electrode. A perforated aluminium diaphragm is interposed between the aluminium and iron electrodes, and the aluminium electrode is insulated from the surrounding aluminium diaphragm by a porcelain sleeve at the top.

When the electrodes were connected to a source of alternating current, a current of 9 amperes, as indicated by a direct-current instrument, was passed through this cell, and after some time globules of fused sodium appeared on the surface. By operating the cell for several days, a considerable quantity of metallic sodium was collected. It was found that careful regulation of the temperature was necessary to pro-

duce a large yield, but, other than this, the cell required no attention. At the end of the run the aluminium electrode showed almost no corrosion, the only indication of it being at the top, at the point where the aluminium was in contact with the porcelain. As a result of a run to determine the amount of corrosion of the aluminium, it was found that an electrode 1.5 inches long and 0.5 inch in diameter lost about one-half gram during a run of 50 ampere-hours. The sodium, upon being liberated, rose to the surface of the liquid, and was prevented from diffusing over the other electrode by means of the aluminium diaphragm.

To determine the effectiveness of the aluminium as an electrolytic valve, current and pressure curves were obtained by means of a Blondel oscillograph. These measurements showed the existence of a small leakage current representing a loss of energy which is wasted unless its heating action is useful in maintaining the cell at the proper temperature. From the curves plotted as results of these measurements, the ampere-hour efficiency was determined to be 73 per cent. The alternating pressure wave form was peaked, while from previous measurements it is proven that a sinusoidal or flatter wave form gives a higher efficiency, so that a higher efficiency of 79 per cent can be realized under other conditions.

The aluminium diaphragm is considered as a new feature. Prof. Burgess has suggested that in its use its property to act as an electrolytic valve may be utilized; the perforations in the aluminium diaphragm may be small and at the same time allow a high current density without the current passing through the aluminium. In the aluminium diaphragm employed in the experiments, no corrosion occurred except at the surface of the electrolyte, where the diaphragm projected from the fused salt; there was a slight corrosion at this point, which could probably be accounted for by the absorption of moisture by the electrolyte when it was allowed to cool.

The author thinks that the same method of operation of an electrolytic cell might be applied for obtaining various electrolytic products other than sodium. While the current efficiency is less than if a direct current be employed, this loss may be partially balanced through avoiding the losses of a rotary converter, required if the supply mains give alternating current.

Electrolysis of Water.

Dr. Joseph W. Richards and Mr. Walter S. Landis then presented a paper in which they give an account of their continued investigation in this field, a first paper on the same subject having been presented at the New York meeting of the society. (See Electrochemical Industry, May, 1903, p. 316.) In their former paper they showed the application of Ohm's law alone to dilute sulphuric acid for voltages up to 3.5 volts. The authors found that their former apparatus in which they used a tube 8.75 long to get a high resistance was unwieldy; they modified it, producing high resistance by the use of short capillary tubes. The cell used in their new experiments consists of two vessels containing the electrodes and connected with each other by a capillary tube, the length of which can be varied to obtain the required resistance.

The authors found that there are two very important factors to be taken into account, viz. the current used and the size of the electrodes. Probably, these two factors are not entirely independent of each other, but the authors had not the means at their command to determine this relation.

The size of the current which can be used depends apparently on the amount of decomposition which can be taken care of by the dissolved gases in the solution. On account of the very small amount of diffusion which can possibly take place within the cell used, the diffusion current could be left out of consideration. The current was regulated by the resistance interposed by the cell, which could be varied to suit the electrolyte used. The size of the electrodes is also an important factor. There seems to be a certain minimum size which is necessary in order that the products of decomposition may be taken care of (recombined) as fast as they are formed.

The results of the experiments of the authors when plotted in form of curves show the curve representing the current as function of the applied volts to be a straight line, and are mainly in very good agreement with the numerical values calculated from Ohm's law on the basis of Kohlrausch's conductivities of solutions. The authors think that on account of this agreement, this method may be of use in determining specific resistances of electrolytes from which oxygen and hydrogen are evolved under ordinary conditions. It is convenient, inasmuch as it allows the employment of direct current, requires no resistance in the circuit other than that of the cell or adjustment of the same, and the required calculations are easily performed. The conditions which must be observed in using this method, are: The current must be kept within the limit of that which can be completely depolarized by the gases in solution in the electrolyte; the electrode surface must be large enough to allow this depolarization to take place simultaneously with the decomposition, and the current readings are the maximum values obtained immediately on closing the circuit, the electrodes being free from polarization before connection is made.

The smaller the electrodes which are used, the stronger is the polarization. A very interesting result obtained by the authors in their further investigation is that an evolution of gas may be obtained at a voltage between 1.15 and 1.12 at a small electrode when opposed to a large electrode, and that this is true for both oxygen and hydrogen. At the large electrode there is no gas development, but the gas which would be evolved there is taken care of by the gases dissolved in the solution; the large electrode surface means that there are enough dissolved gases in contact with it to act as depolarizer. The authors also studied the diffusion current, their results agreeing well with those of Bigelow.

In the discussion which followed, Mr. C. J. Reed, in a sarcastic mood of mind, suggested the term "undervoltage" for the fact that gas is produced with a low voltage at a small electrode when opposed to a large one. He thinks that in this case the large platinum electrode forms a compound and thus acts itself as depolarizer.

Mr. Hering asked what was the exact time when the authors took their readings, and considered this to be very important, as the values of the readings taken depend largely on the time when they are taken. Dr. R. Gahl replied to Mr. Reed that if he wants to use the term undervoltage for the phenomena in question, it would be not at all analogous to the customary term overvoltage; overvoltage means the surplus of voltage required for the development of hydrogen at a cathode of a certain material over the voltage required at platinized platinum, all other things being unchanged; thus, the overvoltage is a property of the material and platinized platinum is taken as standard, to have a convenient zero point for the scale of overvoltage.

Dr. Richards, in reply to Mr. Reed, said that he had found no chemical change of the large platinum electrode in the experiments in which it was opposed to a small one. In reply to Mr. Hering, he said that the readings were taken at 7 seconds after closing the current, because this was the time required for the needle of his instrument to come to rest. The constancy of the readings prove that they are not accidental.

Saturday Session.

Spark Discharges Through Water Vapor.

A paper on this subject was presented by Mr. F. Austin Lidbury. The author referred to the fact that the chemical phenomena which accompany the discharge of electricity through gases, in comparison with those connected with the passage of electricity through solutions, have received scanty attention from investigators. It is well known that many compound gases suffer decomposition to a greater or less extent

by the discharge of electricity through them, and no less well known that an actual separation of the constituent gases, bearing at least a superficial resemblance to the process of electrolysis in liquids, occurs in certain cases. In the majority of these cases the evidence of separation is purely spectroscopic. The investigation of such separations from the electrochemical standpoint has, however, been meager in extent, and practically confined to the single case of water vapor.

From experiments made by Perrot in 1861, the decomposition of compound gases appeared to be similar to the electrolysis of solutions. This view is, however, disproved by the experiments made by the author in conjunction with Mr. D. L. Chapman. In the results obtained two very peculiar phenomena were observed. First, the separated quantities of hydrogen and oxygen in a discharge tube were far greater than were simultaneously obtained from a voltameter (nickel electrodes in caustic soda solution) in the same circuit. Second, in the partial decomposition of water vapor by the electric discharge the hydrogen and oxygen liberated tended to separate and to take up different positions in the tube, the hydrogen collecting at both anode and cathode, and the oxygen in the middle of the tube.

At present there seem to be far too little data for the construction of a satisfactory theory to explain these results, but it is to be noted that Thomson has brought forward some evidence which points to the possibility that hydrogen ions may carry either a positive or negative charge. He observed that a capillary tube containing hydrogen, on the passage of the spark, gave spectra at the anode and cathode, in which the relative brightness of the lines differed. An assumption of this kind might explain the unexpected behavior of hydrogen described above. Facts, however, rather than hypotheses, are what are needed in this particular branch of electrochemistry.

Metallic Diaphragms.

A note on this subject was presented by Dr. Eugene A. Byrnes, and in absence of the author, it was read by Mr. C. P. Townsend. In his researches on carbon cells, with fused electrolytes (Electrochemical Industry, October, 1902, p. 58) he had used a diaphragm consisting of crushed magnetite mixed with Portland cement, and enclosed between perforated iron plates. This diaphragm is suitable for use in fused sodium hydroxide.

Many other metals may be used for such a purpose, as it appears that various conducting materials become poor conductors when used in a finely powdered form; the higher the resistance, the smaller is, of course, the liability of the diaphragm to act as a bipolar electrode. These grains may be either mixed with an inert binder, like silicate of magnesium or calcium or ferrous hydrate, and molded into a self-supporting diaphragm, or they may be used without a binder and enclosed between perforated metal sheets. For cells with a horizontal cathodic surface, a floating diaphragm may be employed.

The paper was not discussed.

Electrolytic Dissociation Theory.

The general discussion of the electrolytic dissociation theory was then opened, three papers, by Messrs. Reed, Richards and Roeber being read as part of the discussion.

The Theoretical Properties of Ions in Solutions.

As an introduction to the general discussion, a paper on the above subject was presented by Dr. E. F. Roeber. The author referred to the method of physical analogies or mechanical models for representing or illustrating one set of facts by another familiar set of facts. This method is in extended use in all fields of physical science, and the electrolytic dissociation theory should be considered from the same point of view as a model representing the phenomena in solutions which are electrolytes, by the model of traveling ions to which certain properties are attributed in order to suit the facts; the electrolytic dissociation theory thus resolves electrolytic phenomena into a mechanics of ions.

Faraday's law states that if n is the change of valency of the element reduced at the cathode or of the element oxidized at the anode (or if one uses Prof. O. T. Johnson's notation, if n is the number of positive bonds lost or gained by one atom at the cathode or anode, respectively,) then the quantity of the element reduced or oxidized by the passage of a amperes for t seconds is $0.0000104\ at \div n$ gramatoms. If the fact of oxidation or reduction at the electrodes is represented by the model of traveling ions a charge of 96,600 positive or negative coulombs must be attributed to each positive or negative gramion. This is the only property of ions which may be derived from Faraday's law. Concerning the nature of the charge the theory is absolutely at liberty to stipulate it, in order to make the model agree with the facts. The author referred to Nernst's view of an ion being a saturated compound of an atom (or group of atoms) with one or more positive or negative electrons. Concerning the energy change from ion to atom we cannot deduce anything from Faraday's law.

To complete the model of traveling ions, it is necessary to find a method by which it is possible to determine what are the ions in a given case, and which is the speed with which each ion travels. The solution of this question was given by Hittorf by studying the concentration changes at the electrodes during electrolysis. Kohlrausch then found the law that in an infinitely dilute solution each ion has a certain characteristic mobility which is independent from the other kinds of ions present in the solution.

The electric charge and the mobility are the two properties which must be attributed to the ion to describe all phenomena in a uniformly concentrated, infinitely dilute aqueous solution. If the solution is not uniform or not of uniform concentration throughout, the fact of the osmotic pressure must be taken into account. Nernst's theory of diffusion and of concentration cells is based on the following assumptions only: That any ion travels with a speed equal to its mobility multiplied with the force acting on it, and that this force is the resultant of two kinds of forces, the electric and osmotic: the electric forces act according to the laws of electrostatics, each n—valent gramion being charged with $96{,}600\ n$ coulombs; the osmotic forces act according to the laws of osmotic pressure which are the same as those of the pressure in gases. That these are all assumptions made concerning the properties of ions, is clearly seen from the fundamental differential equations on which the theory has been based by Planck. The author remarked that from thermodynamics alone we cannot derive new properties of ions; to apply the principles of thermodynamics to dilute solutions, we make distinct assumptions concerning a dilute solution, which find their expression in the equations for energy, volume and entropy.

The model is complete for infinitely dilute solutions, and for this case it has been found to agree absolutely with the facts. All discrepancies which have been discovered between theory and facts refer to more concentrated solutions, for which Arrhenius has developed the model that only a distinct part of the dissolved molecules is ionized, and that only these ions are "active;" he attributes to these active ions the same properties as in infinitely dilute solutions, i. e., he assumes that their charge *and mobility* remain unchanged. The trouble is that the fundamental point of this model—the determination of the degree of ionization—is also its weak point, different methods giving different results for the value of the degree of ionization as has been shown especially by Kahlenberg. Nevertheless, even for more concentrated solutions Arrhenius' model represents an approximation to the truth and has proven very useful in many respects. The ions are tools for scientific progress, and a tool should not be depreciated because it is not perfect.

General Discussion.

The general discussion was then opened by Dr. Wilder D.

Bancroft. After the electrolytic dissociation theory had carried the chemical world by storm, new researches were made along two different lines. One set of experimenters searched for further substantiation and found that the scope of the theory may be extended much more than was probable at first; they have been very successful and believe in the theory now more than ever. The other set of experimenters, notably Kahlenberg, searched for the limitations of the theory; they have also been very successful and have shown that many generalizations formerly made are not justified by the facts. The electrolytic dissociation theory is strictly correct only for infinitely dilute solutions. The trouble with the opponents of the theory is that they have been so far unable to present an exact alternative theory.

Dr. Bancroft then referred to the fact that the dissociation theory had been originally proposed, because the molecular weights in solutions were experimentally found to have abnormal values. He emphasized that the experiments really made do not justify such a sweeping statement; its correctness rests on the assumption that the heat of vaporization is the same for pure water and, for instance, for sodium chloride; but this has never been proven by experiment. A similar apparent abnormal molecular weight was found for sodium in mercury, and was later explained, but not as being due to dissociation. Dr. Barnes is making now very exact measurements in this direction, to clear up this fundamental point.

Dr. Bancroft said that while Dr. Kahlenberg thinks he can explain everything by the affinity between solvent and solution, he has not yet developed an exact theory. It is, however, quite possible that a modification of the theory will be the outcome. The theory has already undergone modifications; early supporters of the theory thought too much of the analogy between a solution and a gas and forgot that, after all, a solution is a liquid.

Mr. C. J. Reed presented a list of those points in which he believes the electrolytic dissociation theory to be a failure. He claims that electric charges are always sources of energy, energy being evolved when a discharge takes place; on the other hand, when ions change to atoms in electrolysis, they never give up energy, but always absorb energy from an outside source. He believes that here is a fundamental inconsistency in the theory. He also thinks that the theory does not account for the electrolysis of fused electrolytes; he asks why should some part of a uniform fused salt (containing nothing else) be ionized. He referred to the experiments described by him before (Electrochemical Industry, October, 1902, p. 61), in which he observed concentration changes which he believes to be in contradiction with the theory. He ridiculed the description of the theory as a model applying for infinitely dilute solutions only. Finally he referred to the numerous investigations of Kahlenberg, and especially his experiments on instantaneous chemical reactions in non-electrolytes; he believes these experiments have proven one of the foundations of the theory to be wrong.

Mr. F. A. Lidbury replied to some of the objections raised by Mr. Reed. Kahlenberg's experiments on instantaneous chemical reactions in non-electrolytes do not contradict any fundamental part of the dissociation theory; they only prove that while the facts appear to show an intimate relation between chemical action and ionization in aqueous solutions, it was wrong to generalize this and apply it to other solutions for which no proof had been given. Concerning fused electrolytes he sees no reason why they should not be ionized just as well as pure water is ionized.

Dr. W. Lash Miller gave a brief account of difficulties which he has encountered in a recent investigation. To determine the nature of the ions in a certain case he used Ostwald's dilution law and tried then to calculate the transport numbers, but they did not agree with the facts; he does not know yet how to explain the discrepancy.

Prof. Henry S. Carhart said that Prof. Bancroft's statement of the present situation had been very fair. He considers the electrolytic dissociation theory as a very useful working hypothesis which has led to the detection of a large number of new facts. On the other hand there are very serious objections and quantitatively there are many discrepancies. He does not like the name electrolytic dissociation, because the ions are assumed to exist as ions before any electrolysis takes place. He thinks further investigations will lead to the evolution of a modified or new theory.

The Thermochemistry of the Dissociation Theory.

A theoretical paper on this subject was presented by Dr. Joseph W. Richards as a contribution towards the discussion. He discussed the subjects of the ionization heat, heat of formation and heat of neutralization, as seen from the standpoint of the theory and from the standpoint of thermochemistry or chemical energetics. His principal thesis was that thermochemistry has established the law of the additive nature of the heat of formation of salts, reckoned to dilute solutions; that this points to each element possessing a thermochemical constant, which is the amount of heat energy which it gives off in the act of going into combination, independent of what other element it combines with, and that the element, when in the state of combination is of lower intrinsic energy than when free, by this thermochemical constant.

The rule of the heat of formation of salts being the sum of the thermochemical constants of their constituents applies approximately only to solid salts, but with almost complete accuracy to salts dissolved in dilute solutions. Therefore, the salts in dilute solutions are the most perfect types of complete "combination" which we possess. Thence results the conclusion that whatever electrolytic dissociation or ionization may be, it is most certainly *not* a resolution of the compound into its constituents or a decomposition of the compound; on the contrary, it is probably a process which brings the constituents into their most perfect state of "combination."

A similar conclusion is reached by regarding the heat of solution of salts. The solid salt is formed from its elements with a large development of heat; but dissolving it in water in excess leads to but a small development of heat, or sometimes a small absorption. Thence it results, that in the dilute solution the compound must be very much nearer in its molecular condition to the solid, undissociated salt, than to the free elements from which it is composed. Therefore, the ionized molecule (whatever that condition may be) is a condition of the *compound*, and not a condition of its constituents. The completely ionized or electrolytically dissociated salt is as much the *salt* or compound as before ionization; sodium chloride in dilute solution is still sodium chloride, as truly as in any other condition. The mere act of solution, with its accompanying ionization, is no destruction of the compound *per se*, because the energy of decomposition has not been absorbed in the act of solution. Therefore, the dissolved salt is still the compound.

A similar conclusion is reached by regarding the heat of dilution of solutions. In concentrated solutions, a salt may be ionized only a few per cent, as indicated by the usual tests. By diluting sufficiently it becomes completely ionized. But heat is usually evolved in dilution, in small amount; sometimes a little is absorbed. This heat of dilution is, however, but a very small proportion of the energy of formation of the compound; therefore, the electrolytic dissociation or ionization of the molecule, whatever it may be, is not a decomposition or destruction of the compound. The constituents of the salt are as much in the combined condition, and constitute as really a compound, in the ionized as in the un-ionized condition.

The *heat of ionization*, if there is really such a quantity, can only mean the energy absorbed in converting a dissolved molecule into dissolved ions. This quantity cannot be the heat of solution of the solid salt, because that necessarily includes the latent heat of fusion of the solid material passing into the

liquid condition, if not possibly also its latent heat of vaporization, since the salt in dilute solution exerts osmotic pressure quite analogous to a gaseous pressure. Neither is it certain that it can be derived with certainty from the heat of dilution, because there is, in many solutions, definite physical and thermal evidence of the formation of definite hydrates in solution, and their subsequent destruction or modification on dilution. Therefore the heat of ionization must not be confounded with the heat of dilution, although, if it is a real value, it is algebraically included within the dilution heat.

The author protested vigorously against Ostwald's use of the term *heat of ionization* as the heat evolved in the passage of free elements into the state of ions in dilute solution, or, rather, into constituents of ionized molecules. This change is really, from the author's point of view, the passage of the elements from the free into the perfectly combined condition, and therefore these *heats of ionization* (Ostwald's), are nothing but the thermochemical constants of the elements, evolved *when going into* combination. Such a use of the term *"heat of ionization"* is unfortunate and very misleading. As used by Ostwald, it is identical with the heat of formation measured thermochemically, and, therefore, an entirely different quantity from that required to ionize a dissolved molecule into ions. Even Ostwald himself would admit that since the sum of the "ionization heats" of two elements equals the heat of formation of their compound, the elements in the state of ions must be perfectly combined, as the chemical compound. This misleading, if not sophistical, use of this term would tend to the following erroneous conclusions on the part of students of electrochemistry: "Ionization heat" is equal to formation heat, therefore, ionization or electrolytic dissociation is really a decomposition of the compound into its constituents. The fallacy of such reasoning is evident when we consider the double meaning which Ostwald attaches to *"ionization heat."*

An interesting application of the principles so far explained was then made, by a consideration of the "heat of neutralization." In dilute hydrochloric acid we have H and Cl in the combined state, each having contributed its thermochemical constant towards the heat of formation of the HCl. Similarly, dilute NaOH contains Na and OH, both in the combined condition. After neutralization, only Na and Cl remain in dilute solution, the H and OH have become liquid water. But since the H and the OH were both in the combined state before neutralization, and also after, the heat of neutralization cannot be the thermochemical heat of combination of H and OH. We cannot write the equation (H, OH) = 13,700 calories as a thermochemical equation; and the oft-repeated statements that the neutralization constant is simply the heat of union of H with OH to form H_2O, as a chemical act of combination, are entirely wrong.

What, then, is the source of the neutralization heat? The author's view is that it can only be physical; that since the H and OH, occurring as HCl and NaOH before neutralization, exerted in that condition osmotic pressure analogous to gas pressure, they may be considered as having changed merely from combined H and OH in the gaseous condition into combined H and OH in the liquid state, a change entirely analogous to condensation of vapor to liquid water. Calculating the energy required to convert liquid water into gaseous molecules exerting a pressure (osmotic) of 6.1 atmospheres, and adding to this the work which would be evolved in the halving of the osmotic pressure of the NaCl molecules (after neutralization the Na and Cl are in double the volume that they were before), the physical change calculates up to 13,430 calories, which accounts almost exactly for the neutralization constant, and appears to conform the views of the author respecting the *identity* of the *"ionized"* condition with the thermochemical *combined* condition of the elements.

The author concluded that on this account the "ionized state" should be considered to be rather a state of combination than of dissociation.

Berthelot's Law Relative to the Electromotive Forces of Cells Based on the Reciprocal Action of Saline Solutions and Soluble Electrolytes.

A paper on this subject by Mr. C. J. Reed was another contribution to the discussion. He referred to a law recently announced by Berthelot, as follows: "When a base acts upon an acid, the e. m. f. developed is the sum of the e. m. fs. developed by the reaction of the corresponding salt separately upon the acid and upon the base. The reacting solutions are supposed to be dilute, in equivalent proportions, and to give rise to no separation of gaseous or insoluble products, and to undergo no progressive change in their internal constitution other than neutralization."

Mr. Reed discussed in detail the experimental proofs advanced by Berthelot, and showed that they are absolutely unsuitable to prove this law. He then claimed that there is no experimental evidence anywhere on record that there exists really an e. m. f. at the junction of two electrolytes. All measurements are made with the use of electrodes, and the e. m. f. at the junction of electrode and electrolyte cannot be eliminated from the total e. m. f. measured. He considers the cells used by Berthelot as concentration cells.

Dr. W. S. Weedon, referring to Dr. Richards' paper, said that the state of combination of a dissolved salt must be different from the ordinary state of combination; ionization may not mean complete separation, but the ions must be independent of each other to some extent. Mr. Alfred H. Cowles said, concerning the energy relation, that it is necessary to consider the energy of the total system—solvent and solute—as a unit.

Dr. H. M. Goodwin spoke of the various fields in which the electrolytic dissociation theory has proven to be useful, and referred to the colors of solutions as explained by the theory. He then said that when investigations go along, one must expect that things come up which don't agree with the theory; this is the way in which a theory is evolved and improved. Concerning Dr. Richards' calculation of the neutralization heat, he thinks it is simpler to assume according to the dissociation theory that the neutralization of an acid by a base corresponds to the combination of the hydrogen ions of the acid with the hydroxyl ions of the base, forming water. Dr. Richards replied that the advantage of his theory is that it enables him to calculate the neutralization heat.

In the following we give an alphabetical list of all members and guests who registered at the meeting.

Charles E. Acker, Niagara Falls; Robert H. Aiken, Winthrop Harbor, Ill.; Edward L. Anderson, Mrs. E. L. Anderson, St. Louis, Mo.; I. A. Andrew, Orange, Conn.; Harry E. Baer, Mrs. M. L. Baker, New York; Wilder D. Bancroft, Mrs. Bancroft, Ithaca, N. Y.; Charles W. Barnaby, New York; I. Baum, Ithaca, N. Y.; Frederick M. Becket, P. McN. Bennie, S. D. Benoliel, Niagara Falls; Miss M. Bent, New York; Henry S. Blackmore, Mount Vernon, N. Y.; George Fred. Brindley, Niagara Falls; William Hand Browne, Jr., New York; C. F. Burgess, Madison, Wis.; R. E. Burkett, Brooklyn, N. Y.; Roy Call, Niagara Falls; Henry S. Carhart, Ann Arbor, Mich.; Charles A. Catlin, Providence, R. I.; Miss Grace Adele Clark, Brooklyn, N. Y.; George B. Cock, Philadelphia; Charles Welles Coit, Niagara Falls; E. A. Colby, Newark, N. J.; C. L. Collins, 2d, Miss Collins, Niagara Falls; Alfred H. Cowles, Cleveland, O.; C. E. Cox, Niagara Falls; L. Douglas Crane, New York; J. S. Crider, Cleveland, O.; J. L. Danziger, New York; H. T. Darlington, Philadelphia; William Dreyfus, New York; Wilber S. Earl, Henry S. Ely, Niagara Falls; C. A. Ernst, Schnectady, N. Y.; Miss Fenner, Providence, R. I.; Francis A. J. Fitzgerald, R. E. Fowler, S. P. Franchot, Niagara Falls; Rudolf Gahl, Mrs. Gahl, Philadelphia; D. E. Golds-borough, Lafayette, Ind.; H. M. Goodwin, Boston; A. Monro Grier, Charles M. Hall, S. F. Hall, Niagara Falls; Louis P. Hamilton, Dunbar, Pa.; George R. Harlow, Pittsburg; William D. Harris, Philadelphia; M. Hartwig, Buffalo; F. W. Haskell, Niagara Falls; Charles Haslwanter, Brooklyn, N. Y.; Carl Hering, Philadelphia; F. W. Higgins, Niagara Falls; B. H. Hite, Morgantown, W. Va.; Norman Holland, W. S. Horry, Niagara Falls; George M. Howard, Philadelphia; H. A. Irvine, Niagara Falls; Otis C. Johnson, Ann Arbor, Mich.; Woolsey McA. Johnson, Iola, Kan.; W. A. Johnston, Princes Bay, N. Y.; Miss M. S. Kennedy, Morristown, N. J.; A. E. Kennelly, Cambridge, Mass.; A. A. Knudson, New York; Mrs. A. A. Knudson, Brooklyn, N. Y.; R. N. Kofoid, Joseph Kuhn, Niagara Falls, Miss C. A. Lee, Rochester, N. Y.; Miss M. L. Lee, Weedsport, N. Y.; E. B. LeMare, Manchester, Eng.;

J. Austin Lidbury, Niagara Falls; James Locke, Boston, Mass.; Henry M. Loomis, D. R. Lovejoy, George F. Lull, Mrs. G. F. Lull, Niagara Falls; J. MacMahon, La Salle, N. Y.; Cloyd Marshall, St. Louis, Mo.; John A. Mathews, Syracuse, N. Y.; H. T. Matthew, New York; Max Mauran, Niagara Falls; W. Lash Miller, Toronto; I. J. Moltkehausen, Perth Amboy, N. J.; C. H. Moritz, Niagara Falls; Henry G. Morris, Philadelphia; William L. Nadolsky, New York; Henry W. Newton, Buffalo; R. I. Nunn, Savannah, Ga.; Ross Phillips, Charles Pretzfeld, W. B. Rankine, G. R. Raynor, Niagara Falls; C. J. Reed, Philadelphia; Joseph W. Richards, Bethlehem, Pa.; I. C. Roberts, Niagara Falls; E. F. Roeber, New York; Ashmead G. Rodgers, Niagara Falls; Marcus Ruthenburg, Michael Sack, Lockport, N. Y.; P. G. Salom, Philadelphia; L. E. Saunders, F. E. Schmitt, Niagara Falls; George P. Scholl, Philadelphia; Charles T. Scott, Pittsburg, Pa.; Edmund S. Smith, E. C. Sprague, Niagara Falls; T. E. Steere, Niagara Falls; H. H. Stock, E. M., Scranton, Pa.; S. W. Stratton, Washington, D. C.; Maurice deKay Thompson, Jr., Boston; Elihu Thompson, Swampscott, Mass.; Clinton P. Townsend, Washington, D. C.; R. A. Trasch, New York; A. Van-Winkle, Newark, N. J.; Chas. F. Vaughn, Niagara Falls; Miss Vaughn, Providence, R. I.; Alois von Isakovics, New York; W. H. Walker, Boston, Mass.; A. Sydney Warren, Buffalo, N. Y.; Wm. S. Weedon, Mrs. Wm. S. Weedon, Schenectady, N. Y.; Sam'l Weil, R. H. White, Niagara Falls; E. H. Whitlock, Cleveland, O.; Henry Wigglesworth, New York City; McKenzie Williams, Toronto; J. M. Wills, Akron, O.; J. Rattray Wilson, R. A. Witherspoon, Niagara Falls; H. H. Withey, St. Louis, Mo.; Ira H. Woolson, New York; A. J. Wurts, Pittsburg, Pa.

VISITS TO PLANTS.

Visits of plants were made on Thursday, Friday and Saturday afternoon. The following companies had extended invitations to the society as a whole: The power plant companies, the Niagara Research Laboratories, and the National Battery

ELECTROLYTIC LABORATORY, NIAGARA RESEARCH LABORATORIES.

Co. in Buffalo. Groups of individual members visited various other plants, among them the works of the Acker Process Co. and the Electric Lead Reduction Co., and Mr. Ruthenburg's experimental furnace plant in Lockport, N. Y. ELECTROCHEMICAL INDUSTRY has already published detailed descriptions of the power houses (1902, September, p. 12), of the Acker plant (1902, October, p. 54), and of the accumulator type made by the National Battery Co. (1902, December, p. 148). In the following we give brief sketches of the other plants visited. At the plant of the National Battery Co., in Buffalo, Mr. Elmer A. Sperry conducted the visitors through the works; the company had provided refreshments.

NIAGARA RESEARCH LABORATORIES.

The Niagara Research Laboratories represent a new departure in the development of electrochemistry in the United States. The company was founded "to maintain a research laboratory for scientific investigations; do analytical and experimental work for the general public; act as consulting engineers in perfecting or improving existing processes; rent space and power for chemical and electrochemical investigations; to manufacture and sell chemicals and allied products." The officers of the company are Messrs. E. B. Stevens, William B. Rankine, Elmer J. Starr and Fred. M. Becket. The engineering staff consists of Messrs. Fred. M. Becket, R. A. Witherspoon and L. E. Saunders.

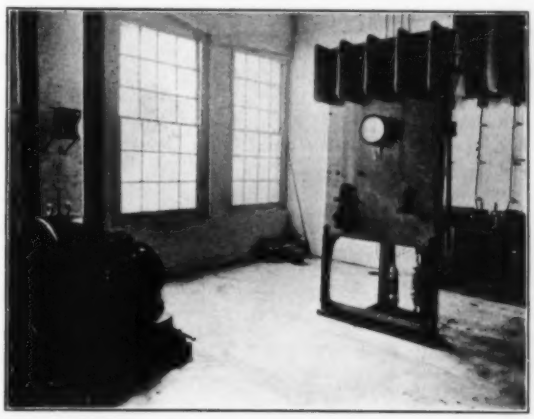
The three-story building of the Niagara Research Laboratories is in the immediate neighborhood of the works of the Electric Lead Reduction Co. The second floor contains the general offices, the library, the electrolytic laboratory, and the analytical laboratory. In order to permit of high temperature electrolytic work, a separately excited 16-kw. generator has

ANALYTICAL LABORATORY, NIAGARA RESEARCH LABORATORIES.

been installed (in the basement), which gives 1000 amperes at 16 volts, or 2000 amperes at 8 volts, thus affording sufficient energy for the development of commercial units. As this generator is supplemented by a storage battery outfit and by rheostats for regulation, electrolytic work of any description may be undertaken.

The adjoining illustration of the electrolytic laboratory (Fig. 1.) shows the table for electrolytic experiments in the back. The surface of the table contains nothing but the binding posts for making the connections, the measuring instruments and the apparatus in which the experiments are made. The switches and regulating rheostats are placed on a shelf underneath, which also holds a number of storage cells to be used when electrolytic work is to be carried on over night.

Fig. 2 shows the room for analytical and general chemical work. It is equipped in a modern way for the analysis of such organic and inorganic compounds as may be met with in commercial work, and with facilities for general chemical research. Among the various apparatus which it contains we noticed a Seward apparatus for determining carbon in ferrochrome, etc., (ELECTROCHEMICAL INDUSTRY, 1903, June, p. 366), and a very convenient electric drying oven, the heating and the regulation



CONVERTER PLANT AND SWITCHBOARD, NIAGARA RESEARCH LABORATORIES.

of the temperature being accomplished by a set of incandescent lamps. A larger drying oven of the same type will be shortly installed. A small adjoining room contains the analytical balances.

The surface plates of all tables in these rooms are of slate,

with longitudinal grooves. They are of historical interest, having formerly been used in the electrolytic cells of the Castner Electrolytic Alkali Co. (which now use concrete tanks); for the present use, the slate plates appear to be ideal.

The ground floor contains converter and transformer plant, the machine shop, the grinding room, and the electric furnace laboratory. Fig. 3 shows the room containing the converter plant. The 16-kw. separately excited direct-current generator which, as mentioned before, gives 1000 amperes at 16 volts, or 2000 amperes at 8 volts, is an Eddy double commutator machine, while all other machines are made by the Westinghouse Co. It is driven by an induction motor, fed with alternating current from the supply mains. The same room contains the controlling board for a 500-hp. transformer, erected in the next room, which changes the alternating current voltage from 2200 to 110 or 55 volts for electric furnace work. A water resistance is installed for regulating the voltage; it is able to carry 8000 amperes, and to consume 50 volts. There is also a smaller transformer of 175 kw.

Fig. 4 shows part of the furnace room. On the left side there is a larger furnace. For furnace lining brown coke and tar is used. At the right hand a smaller furnace is seen; a number of similar ones are to be erected next to it, and all these furnaces are to be arranged in a circle. As seen in the illustration, there is provided a crane with a hanging electrode;

ELECTRIC FURNACE ROOM, NIAGARA RESEARCH LABORATORIES.

by swinging around, this electrode may then be used for any furnace in the circle.

With the view of facilitating the ready setting up of experiments, the machine shop on the ground floor has been equipped with a 21-inch drill press, power forge, a complete set of bench tools, etc. The grinding room contains machinery for the crushing and pulverization of ores, having a capacity of about two tons of rock per day.

Although the entire equipment of the laboratories is at the disposal of experimenters, there have been set aside limited spaces which can be completely isolated, and in which work of a patentable nature may be carried on with the utmost secrecy. Alternating and direct current, gas and water may be had in these rooms, and, if desired, a belted connection with the main line shaft.

Electric Lead Reduction Works.

The visit to this plant reminded us of the untimely death of the chemist of the company, Mr. Alfred J. Weightman, who extended many courtesies to the visitors of the plant a year ago, and who at that time presented to the society an interesting paper on the theoretical questions of the Salom process. An illustrated description of the former installation of this plant was published on page 18 of our September number, 1902; but since that time the general appearance of the electrolysis room has greatly changed. The rows of stacks, each of 11 pans, one placed above the other, have disappeared, since the new form of cell, described above in the abstract of Mr. Salom's paper, has been installed.

There is at present one row of 17 cells in the middle of the room. Each cell looks somewhat like a wheel in a horizontal position. In the present arrangement the cathode which forms the bottom of the cell is rotated, completing one revolution in 1½ hours, which is also the time in which the reduction of galena to lead is completed. The size of the different anode compartments at the top of the cell varies from one compartment to the next in order to diminish automatically the current density, when the reduction becomes more and more complete. The present arrangement has evidently reduced the cost of labor to a large extent. Even under the present conditions in which the feeding of ore to the cathode surface and the scraping off of the reduced spongy lead is done by hand, it is estimated by Messrs. Morris and Salom that three men would be sufficient to do the whole work if the plant were fully equipped.

Some experiments have been made to convert the hydrogen sulphide into sulphuric acid, but the gases are at present mostly wasted. The original intention to utilize the gases which are evolved in gas engines for driving the electric generators has not yet been carried out. It will be remembered that this is theoretically very promising, because the energy of the burning gases is greater than the energy required in the electrolytic process. (J. W. Richards, Transactions American Electrochemical Society, vol. I., p. 931.)

The Plant of the Cowles Co. and the Ruthenburg Iron Furnace.

The experimental iron furnace of Mr. Marcus Ruthenburg is installed in one room of the works of the Cowles Co. at Lockport, N. Y. These works, in a pretty location in a valley between wooded hills, contain much of historical interest. The two Brush machines were considered, at the time of their installation (1886), to be the most powerful generators of the world. The principal output of the Cowles works is at present silicon-copper, used for copper castings. Cuprous oxide dissolves in fused copper, and this is the reason why the making of good uniform copper castings involves great difficulties. These are overcome by adding a small amount of silicon-copper; the silicon combines with the oxygen of the cuprous oxide to form silica. Silicon-copper is used at present to a large extent for this purpose. The original charge is melted in a Cowles furnace of the well-known type with two sliding carbon rods as electrodes. The product of the electric furnace is analysed and then remelted to bring it up to the standard composition.

The Ruthenburg iron process and furnace have already been described repeatedly in Electrochemical Industry (Novembe, 1902, p. 84, and February, 1903, p. 202). The two illustrations given in the above abstract of Mr. Ruthenburg's paper are made from photographs of his furnace in Lockport. They show the horizontal horseshoe magnet, the poles of which are within the slowly revolving rolls. In the small space between these rolls the crushed ore forms a magnetic bridge, and is melted and agglomerated; it then becomes unmagnetic and drops into the soaking pit. The greatest part of Mr. Ruthenburg's recent work has been confined to the study of the best method of producing the reduction in the soaking pit. This occurs by passing hot hydrocarbon gases upwards through the soaking pit (which is about five feet high). The reduced iron is then ready for making steel in a Siemens furnace.

THE PRECIPITATION OF GOLD FROM CYANIDE SOLUTIONS.*

By W. A. Caldecott and E. H. Johnson.

The precipitation of gold from cyanide solutions is a matter which has often been discussed, and a considerable

* A paper presented to the Chemical, Metallurgical and Mining Society of South Africa.

literature already exists upon the subject. At the same time, in spite of its primary importance, in that, after the preliminary operation of dissolving, it is precipitation which concentrates the gold from auriferous material in a solid form, many of the reactions involved are still doubtful. Besides the complexity of the subject, this is no doubt due to the fact that the majority of those engaged in the actual conduct of gold precipitation have their energy fully occupied in the actual running of the plant, and that there is little time available for pure research and extensive investigation, from which an immediate and definite profit cannot be guaranteed. It hence follows that any attempt to explain the reactions which occur must be based on the observation by various workers of various isolated facts. The reactions intermediate between observed phenomena can at present only be explained by that hypothetical reasoning which seems most probable until more is actually known. Though not absolute, such tentative conclusions may be of use, as shown, for instance, in the parallel case of the practical recognition of the validity of Elsner's equation, indicating the utility of oxygen in the dissolving of gold, long before it was proved to be quantitatively correct by Maclaurin.

One view of gold precipitation based on the ionic theory has been dealt with by Prof. von Oettingen, and by Prof. Christy; but, although this view, when fully worked out, may prove the more correct, at present its comparative novelty and the complexity of the reactions of double metallic salts, such as potassium aurocyanide, may render the elaboration of an older and simpler hypothesis of more use to some of us, as a working tool for the time being. This latter view to which we refer is based on the hypothesis that the precipitation of metallic gold from solution may be conveniently and comprehensively regarded as due in practice to the reducing action of nascent hydrogen, which replaces the gold in solution. We are encouraged to consider an explanation of gold precipitation other than the ionic, by the opinion expressed by Bertram Blount, that "the practician * * * can grapple successfully with any problem * * *, irrespective of the precise explanation which may be at the moment most agreeable with the teachings of the ionic hypothesis."

In 1892, B. C. Molloy patented a precipitating agent for gold from cyanide solutions in the shape of an amalgam containing an alkaline metal, which he stated to yield nascent hydrogen when in contact with the solution. Louis Janin, Jr., states in an article on the cyanide process, published in Vol. 1 of the *Mineral Industry* (1903), that "hydrogen is always evolved when the gold is precipitated" in the zinc boxes, and W. R. Feldtmann in his pamphlet (1894) on the cyanide process on the Whitwatersrand surmises that "the accelerating influence on precipitation of excess of potassic cyanide is probably due to generation of nascent hydrogen." But earlier than all these references was the recognition by the first workers on the cyanide process of the fact that effective precipitation was always associated with a "good action," or vigorous evolution of hydrogen bubbles in the zinc boxes.

One of the main features in the precipitation of gold from cyanide solutions is that it exists therein in the form of potassium aurocyanide ($KAuCy_2$). In this state the gold does not form the basic portion of the compound, as it usually does with metals in combination, but is part of the solid radicle $AuCy_2$, which is combined with the potassium as a salt of the hypothetical aurocyanhydric acid ($HAuCy_2$). This compound is similar to cuprosocyanhydric acid ($H_2Cu_2Cy_4$), and is stated to have been prepared in solution in 1878 by C. G. Lindboom (*La Société Chimique*, Tome 29, No. 9.) by addition of sulphuric acid to barium aurocyanide ($BaAu_2Cy_4$). The solid radicle, $AuCy_2$, is exceedingly stable or difficult to entirely decompose, and its tendency to form comparatively soluble compounds renders it difficult of precipitation. The gold may, however, be replaced by H and caused to assume the solid form, or the potassium may be replaced by some other metal such as silver or copper (cuprosum), in which case the gold comes down as an insoluble double metallic cyanide. This latter reaction is, of course, only possible in the absence of free potassium cyanide, in which all cyanides are soluble. In consequence, though equally perfect results can be obtained either way, the former is, so far, the only method for gold precipitation on a large scale, and the latter, involving the destruction of free cyanide, is at present usually confined in practice to one stage in the "precipitation method" of assaying cyanide solutions.

One grain of gold per ton of solution is equivalent to one part by weight in fourteen millions; any method of precipitation which leaves in solution more than one part of gold in ten millions of solutions, cannot, from a working standpoint, be considered first-class; with 2 dwt. solution this would be about equivalent to 97 per cent efficiency.

The precipitation of gold in cyanide solutions is essentially in practice a process of reduction, just as its solution is conversely a process of oxidation. This is obvious if we compare the equations representing in the simplest form the two reactions:

(a) Solution of gold:

$$4KCy + Au_2 + O + H_2O = 2KAuCy_2 + 2KOH.$$

(b) Precipitation of gold:

$$2KAuCy_2 + 2H + 2KOH = Au_2 + 4KCy + 2OH_2.$$

The nascent hydrogen indicated in the latter equation is one of the most powerful reducing agents known at ordinary temperatures. It is readily evolved in cyanide solutions, as, for instance, by zinc shavings (MacArthur-Forrest process), zinc dust, sodium amalgam (Molloy's and Zerener's processes), aluminium-mercury couple (Moldenhauer's process), and various zinc couples (such as zinc-lead, zinc-mercury, zinc-copper, zinc-iron, etc.)

The explanation of electrolytic precipitation of gold from the ionic standpoint may be expressed in the following extract from Macmillan's *Electro-Metallurgy* (1899): "It may be shown that the gold travels with the ion which migrates from cathode to anode, and only the potassium migrates from anode to cathode, yet the gold is deposited only to the cathode. This is due to chemical reaction. The ions of such a cyanide ($KAuCy_2$) are apparently K and $AuCy_2$, the K-ion giving up its charge at the cathode, but immediately attacking the solution in contact with it and depositing, not hydrogen, but gold from the liquid around, because potassium can break up the complex aurocyanide of potassium that is present.

$$KAuCy_2 + K + H_2O = 2KCy + Au + H_2O.$$

Thus gold is deposited at the cathode, not because ions of free gold exist in the liquid, but because potassium is deposited and changes place with the gold in the complex substance $KAuCy_2$ in contact with the cathode. At the same time, gold does not form at the anode, because the ion $AuCy_2$ cannot exist alone in the liquid, but breaks up into cyanogen, Cy, and gold cyanide AuCy, which redissolves in the free potassium cyanide in the solution, reforming potassium aurocyanide. The free cyanogen is then able, with its negative charge, to allow of the passage of another atom of gold to withdraw its positive charge from the anode, and to pass into the ionic condition."

Viewing the equation quoted above from the ordinary chemical standpoint, and assuming the reaction it indicates in this sense as occurring, an intermediate stage may be inserted thus:

$$KAuCy_2 + K + H_2O = KAuCy_2 + H + KOH.$$
$$KAuCy_2 + H + KOH = 2KCy + Au + H_2O.$$

In other words, the intermediate stage corresponds to the equation (b) previously given as indicating the precipitating of gold by nascent hydrogen. On this hypothesis it appears that the nascent hydrogen produced by electrolysis of the water, may also serve to precipitate the gold. In the case of ordinary zinc (really an alloy of zinc with negative elements,

such as lead, iron, carbon, etc.) and of zinc couples, water is also decomposed with evolution of nascent hydrogen and deposition of the gold on the less positive element, and with liberation of oxygen at the zinc. This primary reaction, if viewed from a thermal standpoint, thus:

$$Zn + OH_2 = ZnO + 2H.$$
$$69.0 = 86.4 \qquad -17.4$$

calories indicates a strongly exothermic reaction, or in other words, the hydrogen is liberated owing to the superior affinity zinc has for the oxygen of water; the free potassium cyanide serves to assist the reaction by continually dissolving away the coating of zinc hydrate formed and presenting clean metallic surfaces in contact with the solution.

The same reasoning applies with an amalgam containing an alkaline or alkaline earth metal, or with a magnesium or aluminium couple, or with any metal or metallic couple of which the more electropositive element possesses a stronger affinity for the oxygen in water than does the hydrogen combined with it. The function of the less positive metal in the couple appears to be that of affording a locus, in the shape of innumerable points or roughnesses, for the liberation of hydrogen away from the oxygen simultaneously liberated, at the more positive metal. By this separation the reducing action of the hydrogen, possibly in some cases occluded in the less positive metal, is not interfered with. Mr. MacArthur informed one of the writers that the precipitating efficiency of chemically pure zinc is almost nil. In a suggestive paper read by Mr. Ehrmann before the Chemical, Metallurgical and Mining Society of South Africa in April, 1897, he quotes some very interesting experimental results with zinc and the zinc-copper couple to show that the precipitating efficiency increases with the volume of hydrogen liberated from the solution in the respective instances.

Even if the view expressed in most text books of precipitation being caused by the dissolving of the zinc to directly replace gold in solution be taken it amounts to much the same thing, except that the nascent hydrogen is set free from the water by the potassium liberated by the solution of the zinc instead of by direct decomposition of the water, thus:

$$Zn + 4KCy + 2H_2O = K_2ZnCy_4 + 2KOH + 2H$$
$$2KAuCy_2 + 2KOH + 2H = Au_2 + 4KCy + 2H_2O.$$

or, eliminating similar compounds on both sides, we obtain the equation usually given:

$$Zn + 2KAuCy_2 = K_2ZnCy_4 + Au_2.$$

In all methods of precipitation the liberation of oxygen is a source of trouble; in electrolytic precipitation the anodes constantly waste away, mainly for the same reason as zinc in the MacArthur-Forrest process, and the discovery of a practicable permanent anode is still a subject for research. Besides the waste of material the formation of the oxidation products in the extractor box interfere with efficient working. In case of zinc, as it wastes away, the oxide formed reacts further with the solution yielding various products.

In the Siemens & Halske and electrolytic processes generally the energy required for the precipitation of the gold is originally derived from the burning (or oxidizing) of coal in the boiler-room, whereas in the case of ordinary zinc or zinc couples it is derived from the oxidation (or burning) of zinc in the solution. Hence, in the former case the efficiency of precipitation is not directly dependent upon the strength of the solution, but upon the electric energy applied, whereas in the latter it depends upon the rate of oxidation of the zinc, which increases with the strength of the solution and its cleansing effect already referred to. This cleansing effect may be compared with the dissolving of zinc in sulphuric acid. Speaking of the action of water on zinc, Macmillan says (*Electro-Metallurgy*, p. 349): "The action must stop almost at once, because solid, undissolved and insoluble zinc hydroxide $Zn(OH)_2$ would be formed on the surface of the zinc, and so gradually prevent further contact between the water and the zinc. But when an acid, sulphuric acid, for example, is substituted for water, the action is different, for zinc sulphate ($ZnSO_4$) is soluble in water."

When comparatively strong cyanide solutions (say 0.07 per cent and upwards) are used, the products of oxidation of the zinc dissolve as they are produced, and the efficiency does not decrease. With weak solutions (say 0.01 per cent to 0.03 per cent), however, they do not wholly dissolve, but accumulate in the extractor boxes as a coating on the zinc, thus gradually impairing its efficiency by keeping it from actual contact with the solution until it practically ceases to act. Deposits of finely divided matter from unfiltered turbid solutions act in the same way. The silica found in the zinc boxes is probably mainly due to mechanical causes, such as dust and slight defects in filtering, but may also be partially derived from the charge owing to the slight solubility of silica and silicates in the alkaline solution. Sulphate of lime, produced when treating acid tailings or slimes which require much lime, is also liable to crystallize out from the cyanide solution which is saturated with it upon the precipitating agent.

The deleterious effect of calcium sulphate in solution upon electrolytic precipitation, owing to its small conductivity, has been investigated by Mr. A. F. Crosse. Among other coatings zinc sulphide can usually be detected, and its formation is apparently due to alkaline sulpho-cyanides in the solution, which serve as a carrier of sulphur from the ore or tne commercial cyanide used to the boxes. The reactions seem analagous to those of gold, being probably due to oxidation first and then reduction, as shown in the following typical equations:

(a) $FeS + 6KCy = K_2S + K_4FeCy_6$
$K_2S + KCy + O + H_2O = KSCy + 2KOH.$

(b) $KSCy + Zn(OH)_2 + 2H = ZnS + KCy + 2H_2O.$

It seems possible that selenium acts similarly to sulphur, as at the Redjang Lebong Mine in Sumatra the zinc gold slimes as cleaned up from the boxes were found to contain up to 3.4 per cent selenium (Proc. I. M. M. 23d April, 1903). The presence of common salt and ammonium salts in solution appears to assist precipitation, owing to their slight solvent effect on the zinc hydrate formed. Caustic alkalies should presumably act in this way also, but in practice they seem to have the opposite effect, and to induce the formation of zinc hydrate to a still greater extent than the alkaline zincate formed serves to remove it. The presence of alkaline carbonate in commercial cyanide serves when lime is used to form caustic alkali in the solution thus:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

Mechanical removal of the zinc coatings is effected to some extent by the ordinary practice of washing, and the use of a dilute acid solution for this purpose has also been suggested. A most efficient aid to zinc precipitation would be the discovery of some innocuous solvent for zinc hydrate compatible with cyanide.

Increase of temperature, as shown by Mr. Ehrmann, accelerates precipitation from its natural tendency to promote chemical reactions, with of course increased zinc consumption. In the absence of free alkalies and presence of the hydrocyanic acid, there does not seem much tendency to form zinc hydrate, thus:

$$Zn + 2HCy + 2KCy = K_2ZnCy_4 + 2H.$$

Apart from undissolved zinc hydrate, the general interaction of zinc, potassium cyanide, and caustic alkali may be expressed as follows:

$$Zn_8 + 4\,K\,Cy + 2\,(x-1)\,K\,O\,H$$
$$= 4\,H + K_{2x}\,ZnO_{x+1} + K_2\,Zn\,Cy_4 + (x-3)\,H_2\,O$$

x is a variable quantity, increasing with the dilution of the solution in alkali, and always much greater than indicated in the ordinary formula for potassium zincate, namely K_2ZnO_2. The relative amount of zinc as double cyanide and zincate respectively, in the solution leaving the boxes is possibly in proportion to the respective amounts of free potassium cyanide

and caustic alkali in solution. Hence, on adding additional alkali a certain amount of zinc is transferred from the cyanide combination to the state of zincate and the percentage of free cyanide in solution consequently increased.

It might be expected, from the formation of nascent hydrogen in the boxes, that all dissolved oxygen in the solution leaving them would be removed, and Mr. A. F. Crosse's analyses show this to be the case.

The great barrier to continuously effective precipitation is lack of contact between the precipitating surface and the solution, and owing to the readiness with which this surface becomes coated in various ways, as shown, it is necessary to employ enormous areas to ensure good results. A pound of ordinary zinc shavings exposes about forty square feet of surface, and hence every ton of shavings in the boxes is equivalent to nearly two acres. A ton of solution per cubic foot of zinc per twenty-four hours is equivalent to forty-five minutes' contact, and yet so thoroughly may coatings preserve the zinc from actual contact with the solution that even this rate of flow may with weak solutions have to be diminished to secure good results. The use of lead salts in all dissolving solutions, besides the effect in assisting solution of the gold, apparently owes its advantage of maintaining lengthy efficiency of precipitation with weak solutions to the fact that deposition of lead on the zinc in the boxes enables fresh uncoated precipitating surfaces to be continually exposed. Similarly with cupriferous solutions, lead prevents the copper depositing as a smooth coherent metallic coating on the zinc, which otherwise would be thus shut out from contact with the solution. As might be expected on the assumption that the negative element merely forms a site for disengagement of hydrogen, there appears little difference in the efficiency of the freshly prepared metallic couples, zinc-lead, zinc-copper, zinc-mercury, etc., and advantages of one over the other depend on other considerations. Thus the zinc-mercury couple is brittle and crumbles in use, whilst the zinc-copper tends to yield base bullion. A mixture of lead and zinc shavings has a lengthy efficiency, possibly due to the fact that the zinc hydrate formed does not coat the whole couple to the same extent as with the usual lead-coated zinc shavings.

Hydrogen which has assumed the molecular condition and is visible in the liquid as bubbles is useless for precipitation purposes, the available energy for reduction having been degraded by the self-combination of the nascent atoms into molecules. A vigorous evolution of hydrogen bubbles in the precipitation boxes of any process indicates good precipitation merely since it shows that a corresponding amount of nascent hydrogen, portions of which perform work, is being generated.

Besides nascent hydrogen, however, one or two other means of precipitating gold are available. As chemical precipitants, $AgNO_3$, which forms the insoluble double gold-silver cyanide $AuAgCy_2$ (Crosse), and copper sulphate, reduced by SO_2 from the acidulated solution, which precipitates the gold as the double aurous-cuprous cyanide $Au_2Cu_2Cy_4$ (De Wilde) are rapidly and perfectly efficient.

It is stated that commercial calcium carbide and also phosphine precipitate gold from cyanide solutions. Any such action is probably due to the decomposition of water by substances with such a strong affinity for oxygen.

Many acids and salts effect partial precipitation of the gold in rich solutions, possibly by partly decomposing the potassic aurocyanide, with formation of the hypothetical $HAuCy_2$, which sets free insoluble AuCy to some extent; thus, for example:

$$HCl + KAuCy_2 = KCl + HAu\ Cy_2.$$
$$2HAuCy_2 = HAuCy_2 + HCy + AuCy.$$

A current of H_2S, generated externally and passed through the acidulated auriferous cyanide solution, effects some precipitation. Metallic salts such as $FeCl_3$, $Co(NO_3)_2$, $Pb(NO_3)_2$, or $ZnCl_2$, even when added in excess to gold bearing cyanide solutions, have little precipitating effect when the original amount of gold in solution does not exceed a couple of dwts. per ton (3.4 mgrms. per litre). Oxidizing agents, such as excess of $KMnO_4$, K_3FeCy_6 or HNO_3, used with a view of decomposing by oxidation the soluble $KAuCy_2$ are of small efficiency on solutions low in gold, as also are reducing salts such as $FeSO_4$ or $SnCl_2$, or organic reducers such as formic aldehyde, glucose, glycerine and Fehling's solution. The powerful oxidizing effect, however, due to addition of sulphuric acid, and potassium bichromate to auriferous cyanide solution, seems to thoroughly break up the potassium aurocyanide and precipitate the gold.

The cleansing effect of acids on zinc has already been referred to, and hence it is reasonable that acidulated auriferous solutions, when brought in contact with any metal such as zinc or iron, should rapidly and completely deposit their gold, and this is actually the case.

Freshly burned charcoal acts for a time as an efficient precipitant of gold from cyanide solutions, apparently until the occluded hydrogen, which constitutes about 10 per cent of the gas condensed in the pores, becomes exhausted. It is probable that other materials containing occluded hydrogen would act in the same way.

In general, past experience shows that, apart from acidulated solutions and from processes where electric energy from an external source is made use of, research for a precipitating agent having the following properties would be on the right lines, namely, a body exposing a large amount of surface in proportion to its weight, which gradually dissolves in a solution containing cyanide and possibly some other neutral or alkaline substance compatible with cyanide, with ready evolution of nascent hydrogen. Applying these requisite conditions to filiform zinc or zinc couples and ordinary cyanide solutions, it will be seen that they are fulfilled to a great extent, the main objection being that a comparatively strong solution of costly KCy is required to obtain and maintain the highest possible precipitating efficiency.

The ideal method of precipitation is not only perfectly efficient, but fulfils all the following conditions: 1. It is independent of the cyanide strength of the solution. 2. It presents a large surface for joint contact of the precipitating agent and the molecules of an auriferous compound dissolved in the solution. 3. It concentrates continually the precipitated gold in a limited space. 4. Free cyanide contents of solution are not appreciably lessened by the operation of precipitation. 5. The solution after precipitation must not carry any compound which would interfere with its direct re-use after further addition of cyanide. 6. It allows of ready conversion of precipitated gold into bullion. 7. The apparatus employed must be cheap and simple to install and operate.

IMPORTANT DECISION ON TESLA SPLIT-PHASE PATENTS.—Judge Archibald, of the United States Circuit Court, Eastern District, Pa., has recently handed down a decision in the suit of the Westinghouse Electric & Manufacturing Co. against H. C. Roberts and Sangamo Electric Co., which has an important bearing upon alternating current meters and fan motors. The suit was under the so-called Tesla split-phase patents. The defendants' device against which suit was brought was the Sangamo meter. The court decided that the complainants had satisfactorily proved that Tesla's date of invention preceded that of Farraris and others, and that the device in question was an infringement. Evidence was adduced by the Westinghouse Electric & Manufacturing Co., showing that Tesla's date of invention was several months prior to the Ferraris publication.

In view of the enormous commercial importance which the induction motor now has, the priority of its invention has long been a subject of extended discussion and litigation. It was invented in its principal features independently by Mr. Tesla in this country, and by Prof. Ferraris in Italy, and from this invention dates one of the greatest advances made in alternating-current engineering.

SYNOPSIS OF ARTICLES IN OTHER JOURNALS.

A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.

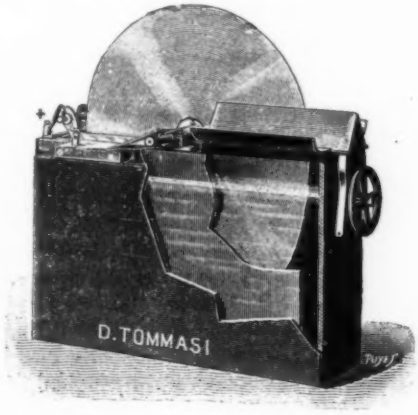
By Carl Hering.

Congress of the Houille Blanche.—In the London *Electrical Review,* September 4, appears the first part of an article, by Marcel Bloch, on the proceedings of the recent Congress of the "Houille Blanche" in France. The term "Houille Blanche," literally "white coal," was first applied in France to designate the motive power obtained from waterfalls. The interesting statement is made that the hydraulic energy of the Alps and the Pyrenees can be utilized to the extent of 10,000,000 hp, there being in use at present in France alone some 500,000 hp of this total. This figure already makes a difference in the consumption of coal in France, and the reserve remaining, it is estimated. will make an annual saving in France of some 200,000,000 of francs which is yearly paid for the importation of coal, amounting to some 13,370,000 tons, out of an annual consumption of 45,200,000 tons. The Congress was convened for the purpose of considering the best means for arriving at this desirable result, and dealt with the legislative, commercial and technical sides of the problem. The author refers to a paper by Picou, in which he drew attention to practical considerations which are to be taken into account in equipping a hydro-electric generating station. According to him there is a necessity of a closer co-operation of the electric and the hydraulic engineer in France for designing such stations. Electrical engineers are warned against too costly installations, by attempting to get exceedingly high efficiencies or too close regulation and costly construction of switchboards. Reference is made by the author more fully to a paper of Gall on the actual status of the electrochemical industries. The first part of the paper deals with the electrolysis of sodium chloride. The different processes for carrying out this electrolysis are touched upon and under the heading of mercury apparatus it is remarked that the Castner and Kellner apparatus is considered the best for this purpose, but although used largely in England and Germany, the Hulin process is better known in France. The latter employs molten lead for forming lead sodium compounds, which are further decomposed by steam. The more modern gravity cells, used in Germany, include neither diaphragm nor mercury, the caustic soda being obtained from electrolysis of sodium chloride solution, which separates it in the cells by means of the higher density of this product, in comparison with the sodium chloride solution. In the opinion of Mr. Gall it is certain that the apparatus now used for the preparation by electrolytic processes of caustic soda and chlorine are more economical than the old-fashioned processes of Leblanc and Solvay, especially when water power is available to give a cheap supply of energy. The output corresponds to a production of 1260 grams of caustic soda, and 1325 grams of chlorine, that is about 400 liters an hour, with a current of 1000 amperes and a maximum difference of potential of 5 volts, which represents an expenditure of 5½ hp per kilogram of soda per hour. He predicts a bright future for the industry, but thinks that on account of the limited demand for bleaching powder in France, a plant producing as much as 10,000 tons of caustic soda, which is not a great total, can hardly dispose of all its chlorine. Other applications of chlorine are being sought out; one of these which would appear to be very suitable, is to the production of tetrachloride of carbon, a liquid body containing 92 per cent of chlorine, with an agreeable odor, and possessing, like benzine and bisulphide of carbon, the property of dissolving fats, but with the advantage of being uninflammable and not forming explosive mixtures with the air. It is stated that on all sides this substance is being experimented with. The paper then touched upon the manufacture of alkaline hypochlorites, it being stated that Hermite's process is the best known. The current intensity is 1000 amperes to 1200 amperes, under a difference of potential of 5 volts; the paper manufacturers are said to be in favor of this process. The manufacture of chlorates is next touched upon, and it is stated that the works at Chedde have recently prepared, with the aid of special and perfected apparatus, an explosive powder, under the name of cheddite, superior to those now in existence. The author states that Mr. Gall laid great stress on the importance of the regulations concerning the production of electrochemical products, especially in regard to the tariffs for transport and the duties paid on them, to enable easy exportation of the material, without which the industry would never be able to exist in the face of foreign competition. Another paper by Boucher deals with the question of cleaning the water from the water courses, before utilizing it in the turbines.

Tommasi's Apparatus for the Preparation of Spongy Lead.—In L'Industrie Electrochimique, August, there is given an illustrated description of Tommasi's apparatus for the electrolytic preparation of spongy lead. It is reproduced in the adjoining figure and consists of a rectangular vat, filled with a solution of the double acetate of lead and sodium. A pair of anodes of lead are arranged, one on each side of a disk-shaped lead cathode, which can be rotated; only a segment of the latter dips into the electrolyte. As the disk rotates that part of it which emerges from the electrolyte passes between two scrapers, which are stated not only to serve the function of scraping the lead off, but also to depolarize the surface of the disk. The lead thus obtained represents a spongy mass, composed of a multitude of small crystals, and is said to be very suitable for storage batteries, and especially those of Tommasi's system. The cost of preparation of 1 ton of spongy lead is said to be 10 francs, which seems surprisingly low.

Light Aluminium Alloys.—Before the recent meeting of the American Society for Testing Materials, Prof. J. W. Richards read a paper on the above subject. He stated that for all purposes where the rolled, drawn or worked pure metal is sufficiently hard and strong, it is advisable to use the pure metal, as it resists alteration by the atmosphere and other corroding agencies better than almost any of its alloys, and better the purer it is. For cast articles and wire, rod or sheet, which are not sufficiently strong or hard when made of the pure metal, the aluminium can be alloyed with small quantities of other metals, which improve it in various ways without materially increasing its specific gravity. The best method of alloying the aluminium with other metals is taken up and described in detail, the use of a flux in melting not being recommended, as it attacks the crucible, and thus introduces impurities into the alloy. Almost all the light, strong alloys are stated to melt easier than aluminium, antimony, however, being an exception, as small quantities of it increase the melting point considerably. Thirty-three per cent of antimony makes an alloy which melts at 230 degrees higher than aluminium, and 250 degrees higher than antimony. As far as the specific gravity is concerned, the alloys with magnesium, 2 to 12 per cent, are the only ones which are lighter than aluminium. Theoretically, 10 per cent of magnesium would make a mixture which should have a specific gravity 0.16 less than aluminium, whereas it is actually 0.24 lighter. This points to expansion taking place during alloying. The molds for castings, the rolling and annealing, the dipping and frosting and the black finishing of the alloys are

then discussed. Prof. Richards then describes the alloys of aluminium with various metals, such as chromium, titanium, manganese, tin, silver, nickel, tungsten, copper, magnesium and zinc. He states that the chromium alloys are being used commercially at present, but that the use of the titanium alloys has practically disappeared, as they are easily corroded. The alloys of nickel with aluminium have not been found advantageous. The use of the magnesium alloys, such as magnalium, is said to be increasing in Europe, but no report of their durability is yet at hand. The Magnalium Gesellschaft, of Berlin, Germany, states that 61,000 lbs. per sq. in. may be obtained in chill castings. Cast in sand the



PREPARATION OF SPONGY LEAD.

same alloy gives 21,400 lbs. per sq. in. The alloy contained 10 per cent of magnesium. Zinc is stated to be the cheapest, and, at the same time, one of the most efficient metals, which improves the mechanical qualities of aluminium. Up to 15 per cent the alloys are malleable, and in castings up to 33 per cent may be used. Casting in chills gives much better results than in sand. It is stated that a commercial alloy for making hard, strong and sharp castings consists of 15 per cent of zinc, 2 per cent of tin, 2 per cent of copper and 0.5 per cent each of manganese and iron. The paper is reprinted in *Metal Industry*, August.

Recovery of Nickel from Scrap Anodes.—The usual practice is to melt scrap nickel anodes in the crucible. BECKWITH, at the recent Convention of the American Foundrymen in Milwaukee, gave an account of how a cupola was used for the purpose. As nickel is more infusible than iron, more coke is consumed, and the charges had to be made accordingly. A ratio of one to one was used for the bed, and two and one-half to one for the charges. The following is the result of one run, which required two heats, the total amount of scrap melted being 875 lbs. The scrap was worth $218.75, the coke used was 640 lbs., valued at $2.25; molder's time, $3; labor, $2, or total cost $226. The yield was 635 lbs. of nickel anodes, which, at 50 cents a pound, made $317.50; then 75 lbs. scrap, worth $18.78, making a profit on the operation of $110.25.—*Metal Industry*, August.

THEORETICAL AND EXPERIMENTAL.

Determination of the Electrochemical Equivalent of Silver.—The most recent determinations of the electrochemical equivalent of silver, by Potier, and Pellat, and Paterson, and Guthe had given the value 0.011192. But experiments of Richards, Collins and Heimrod had led to the belief that this number was too high by about two thousandth (presumably meaning two parts in one thousand). PELLAT AND LEDUC therefore determined to repeat the experiments, following the method used by Potier and Pellat with the following modifications. The voltameter was formed of a hemispherical silver dish, serving as cathode, and having a surplus of 500 sq. cm. It was filled with a normal solution of silver nitrate, neutral towards methylorange. The anode was formed of pure crystalline silver from previous electrolyses, which was contained in a sort of inversed receptacle, and separated from the bath by a sheet of paper between two layers of muslin. The anode surface was about 50 sq. cm., and the current about 1 ampere. The duration of the experiments was two to three hours, and the amount of silver deposited was 8.3 to 12.4 grams. The influence of the various sources of error, as the uncertainty of the beginning and the end of the experiment, the variation of the current, the errors of weighing, washing, etc., were thus considerably reduced. The Daniell cells were replaced by accumulators which gave a remarkably steady current. The circuit comprised a rheostat, an interruptor and a resistance r of about 1.4 ohms, formed by a bare constantan wire dipped into a bath of petroleum. The difference of potential $r\,i$ at the terminals of this resistance was opposed to the electromotive force of a Latimer-Clark cell, and the equality was found by means of a capillary electrometer. The equilibrium was maintained during the whole experiment by very slight adjustments of the rheostat. The regulating period in the beginning did not occupy more than a fraction of a minute. In order to ascertain in absolute value the intensity of the current, the electromotive force of the Latimer-Clark cell was determined For this purpose an absolute electrolynamometer was substituted for the voltameter, and the same Latimer-Clark was opposed to the difference of potential IR produced at the ends of another resistance, R of 4.8 ohms about, constituted exactly like the first one. The coefficient of variation of E with the temperature was carefully determined, and found to be equal to 0.000845. The relation R to r of the resistances, was also carefully determined by many concordant observations. The coefficients of temperature variations of R and r were found very small. The time was measured by a very fine chronometer. All the weighings were corrected for air pressure, and the weights were compared with a gram weight from the International Bureau of Weights and Measures. The average of three well concordant experiments gave 0.011195, and the authors believe that it seems that the total systematic error cannot exceed one-half thousandth. The authors, therefore, consider it as certain that the mass of silver deposited by one coulomb under the above conditions is comprised between 1.119 mg. and 1.120 mg. The comparison of the resistance R with a mercury ohm, placed in melting ice, has permitted the authors to deduce from the above determinations the absolute value of the electromotive force of the Latimer-Clark cell, which has been found to be 1.4334 volts at 15°. Another similar cell gave 1.4337 volts. Two Weston elements gave 1.0169 volts, and 1.0181 volts respecively, the values being expressed in international volts, derived from the international and the theoretical ohm. The paper was presented before the French Academy of Sciences, and is reprinted in *L'Industrie Electrique*, August 10.

Rotation of Liquids in the Magnetic Field.—PROF. DRUDE, the well-known physicist, maintains that theoretically there can be no motion of a diffusing liquid, the diffusion of which takes place vertically to the lines of force of a magnetic field, if there is not generated at the same time an electric current in the liquid. Such a liquid, therefore, does not rotate in a magnetic field, the lines of force of which run radially-horizontally, if the liquid is arranged so that it is insulated, and the temperature of the diffusing layer is everywhere the same, so that no electric current can be generated. As the electromotive force between dilute and concentrated liquids, for instance, H_2O and H_2SO_4, depends, as a rule, on the temperature, electric currents (thermo currents) must be generated, when the temperature of the diffusing layer is not constant, and as a consequence a rotation of the liquid in the magnetic field is produced. For instance, take the case of H_2SO_4 and H_2O, which are carefully super-

posed upon each other in a glass vessel (H_2O above), so that a well defined horizontal diffusion layer is produced. If the rim of the vessel is heated up, say by a coil or a warm bath or a flame, thermo currents must be generated, which rise vertically at the rim of the vessel, flow horizontally for a little distance in the water, then descend vertically in the neighborhood of the center, and return again horizontally towards the rim. If, therefore, this glass vessel is introduced into a space filled with horizontal radial lines of force, directed towards the interior, the liquid seen from above must rotate at the rim in a clockwise direction, and counterclockwise in the center. Experiments which bear out this theory are described by Prof. Drude in the *Zeitsch. f. Eletrochem.*, August 13. In a crystallizing dish of 10 cm. diameter, H_2SO_4 and H_2O were carefully superposed, and the dish was put upon the core of 10 cm. diameter of a large electromagnet, which served as the north pole. The south pole of the electromagnet was formed of a wrought-iron cylinder, 3.5 or 2.6 cm., in diameter, which was arranged ½ cm. above the liquid. When the magnet was excited, a rotation of the liquid took place in one or more directions, according as to whether little or much H_2O had been superimposed on the H_2SO_4. Evidently the initial conditions are very complicated, as considerable heat is generated by the diffusion of the H_2O into the H_2SO_4, which heat will be less at the walls of the vessel on account of the cooling effect of the walls. The liquid must, therefore, rotate counter clockwise at the rim, and the experiment showed this to be the case. But if the rim was heated, the direction of rotation reversed, and finally the whole liquid rotated in the clockwise direction. This is explained by the shape of the magnetic field in this particular case, as the lines of force are vertical in the center, and their horizontal component is very much smaller there than at the rim, therefore the counter clockwise movement in the center, which is to be theoretically expected, does not take place. It was proved, experimentally, that the difference of temperature of the diffusing layer was determinative for the rotation of the liquid, by introducing a needle-shaped thermo-element into the diffusing layer. When the element was moved radially, temperature differences were found, which were parallel to the direction of rotation of the liquid at the same place. For instance, if the measurements were taken from the rim towards the center, and the indications of the thermo-element showed cold, warm, and cold again, the rotations at the same places were left hand, right hand and left hand again. If, finally, a unidirectional rotation had set in, after heating the rim of the vessel, the thermo-element always showed a constant decrease of temperature from the rim towards the center. The rotations which appear in the beginning without heating of the rim, soon disappear, evidently on account of the equalization of the differences of temperature in the diffusing layer; but if the rim is heated, rotation appears again, and always in the expected direction. Drude concludes that Urbasch's experiments, which were made without heating the liquid, only give favorable results in the case of H_2SO_4 and H_2O, on account of the considerable heat produced by the diffusion. with HCl and H_2O in this case, the phenomenon manifests itself only to a very slight degree, and with $CuSO_4$ and H_2O it does not appear at all. When the rim is heated, the rotation becomes very perceptible in the case of HCl and H_2O, but in an opposite direction to that of H_2SO_4 and H_2O. The thermo-electric current between the former combination is opposite to that between the latter. $CuSO_4$ and H_2O showed very small thermo-electric currents, and, therefore, a sensible rotation could not be obtained, even when the rim of the vessel was heated. The experiments do not succeed if the upper pole is not situated above the liquid, but dips into it, and is kept from coming into contact with it by a glass cover. In that case the central parts of the liquid are also cooled off, the same as the layer around the rim.

Electrolytic Separation.—Methods for the electro-analytical separation of manganese from iron; aluminium from iron and nickel; and zinc from iron, are described by Hollard and Bertiaux in *Comptes Rendues*, t. 136, pages 1266-1268, and reprinted in *L'Eclairage Electrique*, June 27. The separation of manganese from iron is one of the most difficult problems of electro-analysis, but, at the same time, a most desirable one, as it enables one to determine both metals at the same time. Manganese, as is well known, is one of the few metals which separate under ordinary conditions as peroxide on the anode, while the iron goes to the cathode. The method which the two authors propose depends upon the addition of sulphurous acid to the electrolyte. The electrolyte is made by adding to a solution of the sulphates of iron and manganese, which may contain a few drops of free sulphuric acid, 5 grams of citric acid, 25 to 50 cc. (according to the quantity of iron present) of a saturated solution of SO_2, and 25 cc. of ammonia of 22° B. It is neutralized by adding sulphuric acid and then made alkaline again with a few cc. of ammonia. The iron is deposited on a platinum cathode with large surface, the anode is a platinum spiral of small surface. Electrolysis is conducted at a temperature of 48°, with a current of one ampere, the volume of the solution being 300 cc. With a suitable proportion of sulphurous acid, the iron is deposited completely on the cathode before the manganese comes down on the anode. The solution is then poured off, the deposit dissolved in 1-5 sulphuric acid and titrated with the usual precautions with permanganate. In order to precipitate the managanese, the solution is again electrolyzed with a platinum anode of large surface, and a small spiral cathode. The temperature of the bath must be between 90 and 95° C., and the current one ampere. The excess of SO_2 is soon oxidized, and the manganese is deposited at the anode, the operation being complete at the end of several hours. The manganese is determined volumetrically, by adding hydrochloric acid, potassium iodide and carbon bisulphide. The chlorine set free by the MnO_2 liberates iodine, which dissolves in the carbon bisulphide. The latter is then titrated with hyposulphite until the bisulphide of carbon is no longer colored pink. The separation of iron and aluminium has been effected by the authors in an analogous way. The metals, in the condition of sulphates, are electrolyzed with the addition of ammonium citrate and sulphurous acid under the same conditions as above. It is said that the effect of the SO_2 is, first, to prevent, during electrolysis, the precipitation of alumina, which might carry some iron with it, and, secondly, the precipitation of iron as basic salts. The separation of iron and zinc has been accomplished in a similar manner with the help of sulphurous acid, the iron being brought into the condition of ferrocyanide of potassium. The solution of zinc and iron, as sulphates, was treated with 25 to 50 cc. of sulphurous acid (according to the quantity of iron present), and nearly neutralized with soda; 15 cc. of potassium cyanide of 20 per cent were then added and, after this, 50 cc. of soda of 15° B. The solution was diluted to 300 cc., and electrolysis carried out in the cold with a current of 0.3 ampere. The zinc, under these conditions, comes down alone, and the iron stays in solution.

Electrolytic Reduction of Unsaturated Acids.—Prof. C. Marie describes, in *Comptes Rendues*, for the meeting of June 2, 1903, reprinted in *L'Electrochimie*, July, a series of experiments, which he conducted, in order to find out whether an absorption of hydrogen could be brought about at the cathode, in the electrolysis of unsaturated organic acids, in order to change them into the corresponding saturated acids. He experimented with aconitic acid, which he wanted to convert into tricarballylic acid. Electrolysis was conducted with different metallic cathodes; with platinum, copper and lead no reduction worth mentioning was obtained. It was necessary to use mercury as cathode, in order to succeed. The experiments were conducted in the following manner. The solution of aconitic acid, half neutralized with soda, is put into a cooled vessel, the bottom of which is covered with mercury, which

serves as cathode. The anode is constituted by a small strip of platinum. The cathodic current density is about 2 amperes per sq. dm. The absorption of the hydrogen is not complete, even in the beginning; there is always a certain amount liberated as such, and, therefore, about twice the theoretically-calculated quantity of current is necessary. The solution is then neutralized by soda, and the resulting tricarballylic acid is separated by copper acetate or nitrate, the copper tricarballylate being insoluble in the solution, which is slightly acid from acetic acid, while the copper aconitate is soluble. After the decomposition of the salt by H_2S, the acid is obtained with a yield of about 60 per cent. The loss is caused by the anodic destruction of the product with the formation of CO_2 and of unsaturated compounds of a disagreeable odor. The destruction is considerably increased when the operation is conducted at elevated temperature or in alkaline solution. On the contrary, the oxidation is nearly annulled if a more stable unsaturated acid is taken; for instance, cinnamic acid. The electrolysis of this acid, under the above conditions, gives hydrocinnamic acid in nearly quantitative yield.

Active and Inactive State of Two Identical Carbon Electrodes in Fused Electrolytes.—The observation that two carbons which, in molten calcium chloride, showed a difference of potential, though they had not been connected to a source of current, led J. Harden to investigate this phenomenon. His results are published in the *Phys. Zeitsch.*, July 15. He thought, in the beginning, that a difference in the electrodes might give rise to the production of thermo-electric currents, but the difference of potential observed seemed too large to be explained in that way. The experiment was then carried out in the following manner. A carbon rod of 5 mm. thickness, 350 mm. long, made from carbon as pure as possible, was first heated in an electrically-heated carbon tube up to 1800°, to drive out any impurities. The rod was then cut in the middle and fixed in a support in such a way that the cut surfaces could be pressed against each other by screws. The outer ends of the rods were connected with a millivoltmeter. The ends which pressed against each other were then brought to a strong, high, white heat by a blast lamp, but the highest obtainable deflection was only 5.5 millivolts. Chloride of calcium was then heated up in a porcelain crucible, and the above electrodes introduced. As soon as the salt began to melt, the galvanometer showed a deflection toward the right and again toward the left; this vaccillation showed itself every time when fresh electrodes were introduced, even when the melt was already fluid. After a short time, however, there manifested itself a steady activity of one electrode, producing a continuous deflection toward one side. The difference of potential increased to a certain point with increasing temperature; after the latter had been overstepped, the potential decreased again. This point was at 650° C. with calcium chloride, and the difference of potential was 0.15 volts. The polarization was so great, however, that if an instrument with only 10 ohms resistance was used, the potential dropped immediately, and it did not make any difference, in this case, whether a larger or a smaller piece of the electrodes dipped into the melt. The indications of the galvanometer were not changed, whether the electrodes were protected from the air during the experiment or not. The phenomenon showed itself not only with calcium chloride, but also, though in a lesser degree, with calcium nitrate. The melting temperature of the salt is not the determining factor for the difference of potential, for if the electrolyte was molten-lead chloride a potential of 0.35 volts was observed, while the temperature was only about 360° C. A mixture of sodium and potassium carbonate gave about 0.04 volts. The distribution of the temperature seems to play an important role, for the amount of the difference of potential varied considerably if the crucible was heated on one side only. The curious fact was, however, established that the activity was greatest at that electrode which had the lowest temperature. If one or the other side of the crucible was heated alternately, the direction of the current was often reversed, but this did not take place with regularity. The author thinks that when chloride of calcium, for instance, into which two carbon rods are dipped, is heated, a chemical reaction takes place in such a way that the carbon combines with the chlorine. On account of the difference of temperature, one electrode is then enabled to take more chlorine ions than the other, which would explain the difference of potential. The fact that the two electrodes were attacked, but one more than the other, seems to him to bear out this opinion.

Silicides of Chromium.—To the three silicides of chromium, which had been described up to the present, namely, $SiCr_3$, $SiCr_2$ and Si_2Cr, there is now added a fourth one, Si_2Cr_3, another product of the electric furnace. The method of preparation of the latter is described by its discoverers, Lebeau and Figueras, in *Comptes Rendues*, séance du 2 Juin, reprinted in *L'Electrochimie*, July. It is obtained by heating, in the Moissan furnace, in a carbon crucible, a mixture of 100 grams of silicide of copper of 12 per cent, with 4 grams of chromium. The time of heating must be four minutes, with a current of 600 amperes at 70 volts. The resulting regulus must have about the theoretical weight. It is pulverized and extracted with dilute nitric acid, alternately with dilute commercial caustic soda, until the action of the two reagents ceases. The silicide, Si_2Cr_3, crystallizes in long quadrangular prisms. Its density is 5.6 at 0°. It scratches glass, but not quartz. Chlorine reacts with it with incandescence at about 400°, giving chlorides of chromium and silicon, bromine attacks it more slowly at a cherry-red heat, and iodine under the same condition has no action. It is unoxidizable in dry or moist air in the cold. Hydrochloric acid gas decomposes it with the production of chromous chloride. Dilute cold hydrochloric acid does not act on it, but the concentrated acid dissolves it very easily, if heated a little; nitric and sulphuric acid do not act upon it, but hydrofluoric acid attacks it in a few moments. The nitrate and chlorate of potassium in a fused state, which react energetically with the carbides of chromium, do not change the silicide, but with the alkaline carbonates it transforms itself rapidly into silicate and oxide of chromium. If a nitrate is added, a mixture of silicate and alkali chromate is formed.

Silicide of Ruthenium.—Moissan and Manchot describe in Comptes Rendues, vol. 137, p. 229, the preparation and the properties of a silicide of ruthenium. If a mixture of 1.5 grams of powdered ruthenium and 7 grams of crystallized silicon is put into a carbon boat in the middle of a tube of the same substance, the mixture rapidly fuses, and the combination takes place. The latter is accompanied by a rapid disengagement of vapors, after which the liquid becomes quiet again, and the experiment is finished. Two or three minutes are required, with a current of 600 amperes, at 120 volts. At the moment of combination a certain quantity of the metal volatilises in the form of a brown vapor. It is important that the current of the electric furnace should be very constant, otherwise the results are not comparable. Under these conditions a well-fused regulus is obtained, which is pulverized, and first treated on the water bath with a solution of caustic soda, and then with a mixture of hydrofluoric and nitric acids. The residue consists of brilliant white crystals, mixed with variable quantities of carborundum, which can be separated from them owing to the difference of specific gravity, by methyl iodide, in which one floats and the other sinks. The same compound can be obtained in a state of greater purity, by heating in the electric furnace, in a carbon crucible, a mixture of 1.5 grams of ruthenium, 15 grams silicon and 5 grams of copper. The reaction takes place with more regularity at the boiling temperature of the silicide of copper, and after the same treatment as above, there is obtained a very well crystallized silicide of ruthenium, corresponding to the formula Ru Si, and free from carborundum. The yield is about 80 per cent of the weight of ruthenium

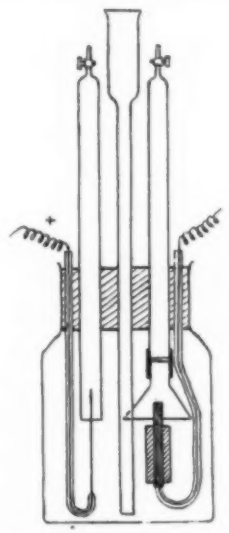
taken. The properties and the method of analysis of this new compound are also described.

Double Carbide of Chromium and Tungsten.—Up to the present time only very few double metallic carbides were known, as, for instance, those of iron and tungsten, iron and chromium, iron and manganese, etc. Moissan and Kouznetzow, in *L'Eclairage Electrique*, August 22, describe the preparation of a new double carbide, that of chromium and tungsten, in the electric furnace. In order to prepare it, a mixture of 100 grams of sesquioxyde of chromium, 45 grams of tungstic acid and 30 grams of petroleum coke or sugar carbon, are heated in the electric furnace, in a carbon crucible for about five minutes. It is important not to use a current of too high intensity, 400 amperes, at 75 volts, being sufficient. A homogenous regulus of metallic appearance is obtained, which is pulverized and treated with hot hydrochloric acid. Then follows a treatment with concentrated ammonia, to dissolve the particles of tungstic acid which are inclosed. The residual powder is washed with water and dried. The double carbide can also be prepared by another method. A mixture of chromium and metallic tungsten, with an addition of a small quantity of sugar carbon in presence of a great excess of copper, is fused in the electric furnace, avoiding as much as possible the carbon vapors of the arc. The proportions are: Tungsten, 7.5 grams, chromium, 10 grams, carbon, 0.2 grams, and copper, 150 grams. The mixture is fused rapidly in a carbon crucible, and the copper is maintained in ebullition for 1 or 2 minutes. After cooling, a metallic homogeneous regulus remains in the crucible, which is treated with nitric acid. The residue consists of small crystalline crusts, of metallic aspect, which are represented by the formula, W_2C, $3Cr_2C_2$.

Specific Resistance of Non-Metallic Conductors of the First Class.—In the *Zeitsch. f. Electrochem.*, August 13 Ferchland gives the results of his measurements of the specific resistance of peroxide of lead under compression. He obtained his material by electrodeposition from a 25 per cent lead nitrate solution, which was kept neutral by the continuous addition of lead oxide or carbonate. With a suitable current density at the anode, of 5 amperes per sq. dm., there was obtained a deposit of almost black color, perfectly dense, and having a glassy lustre. It was very strong, and so hard that it was not attacked by emery. The chemical composition did not correspond exactly to the formula PbO_2, but was very constant, showing about 1.5 per cent of water. The material was obtained in cylinders of 0.35 to 0.36 cm. diameter, and 1 to 6 cm. length, with a hole in the center. A difficulty was found in getting good contacts, until the author utilized the idea of introducing the peroxide rods in a machinist's die tap, for cutting screws. They were insulated from the tap, and the screw of the latter tightened more and more, until the resistance of the lead peroxide rods did not further decrease, or until they broke. The measurement of the resistance was carried out with a universal bridge and a very sensitive galvanometer as zero instrument. The results of the decrease of the resistance with increasing pressure are given. The spec. resistance, in terms of the meter, square millimeter unit, was found to be 29.9 ohms in one case, and 37 ohms in another. The results show a variation from those obtained by Streintz from the compression of powders, being about 13 to 16 times greater. The author attributes this to possible variations in the composition of the electrolytically deposited peroxide of lead owing to differences in the amount of water contained in it. He calls attention to the considerable effect of even the smallest impurities of a body on its conductivity.

Primary and Secondary Batteries.

Peroxide of Manganese Briquettes and Cylinders.—The manganese peroxide briquettes and cylinders for Leclanche cells are very unequal in their qualities. They are manufactured usually by compression of the mixture of the different materials at somewhat elevated temperature, about 100° C. Dr. J. Zellner gives the analysis of several of them in an article on the above subject in the *Centralblatt f. Acc. Elem. u. Automobilenkunde*, July 15, and August 15. He shows further, that the calcination of the briquettes is absolutely senseless, by citing the case of a mixture consisting of retort graphite, 41.67 per cent; peroxide of manganese, 41.67 per cent (of 73.86 MnO_2); tar, 16.66 per cent. The amount of peroxide of manganese was, therefore, 30.8 per cent. After calcination, the mixture should contain 34.6 per cent of peroxide of manganese, assuming that about one-third of the tar remains in the form of carbon. The analysis, however, only showed 14.59 per cent; consequently, more than half the peroxide had become inactive. The author gives as the reason for the fact that so many calcined briquettes appear in the trade that the manufacture of briquettes is often in the hands of people with insufficient knowledge of chemistry. It is also stated, as an excuse, that the peroxide briquettes thus manufactured regenerate themselves in the air, which evidently means that the lower manganese oxide changes partly into the three-four oxide. The author gives the results of experiments which he made on this question, which showed that the manganous oxide, in moderately damp air, hardly oxidizes at all and, therefore, the above regeneration of the briquettes amounts to practically nothing. There is also usually entirely too much peroxide of manganese in such briquettes; as, after a good many years, during which time the zinc rods had been frequently renewed, the average peroxide content was still 80 per cent. As to the most efficient form of using the peroxide of manganese, the author thinks that the best way is to surround the battery carbons by compression with a mixture of finely-powdered peroxide and finely-powdered carbon (graphite). The use of good conducting carbon, for instance, pure graphite and as strong compression as possible will favorably influence the conductivity. Briquettes are best used in the form of thin plates, arranged close to the carbon. The author then gives the method of analysis of the carbon-manganese peroxide briquettes. The analysis, however, is not the only factor for a determination of the quality of a manganese peroxide body, as the depolarising action depends not only on the quantity and quality of the peroxide, but also on the thickness of the grain, the quality of the carbon and the porosity. The author uses the apparatus illustrated in the above figure, for the determination of the quality of a briquette. It consists essentially of a glass jar, closed by a cork stopper, with five perforations. Two measuring tubes provided with stopcocks are introduced through two of these openings, the lower end of one of the tubes being formed by a funnel, so as to catch all the gas which is generated at the peroxide briquette. The middle perforation receives a rather large funnel tube, and through the last two pass the platinum wires for the electric current, enclosed in glass tubes. The positive pole is formed by one of the platinum wires, while the briquette to be tested is connected with the negative wire. The vessel and the measuring tubes are filled with a pretty concentrated solution of sulphate of ammonia. A current of 0.1 to 0.2 amperes from two storage bat-



DETERMINATION OF THE QUALITY OF MANGANESE BRIQUETTES.

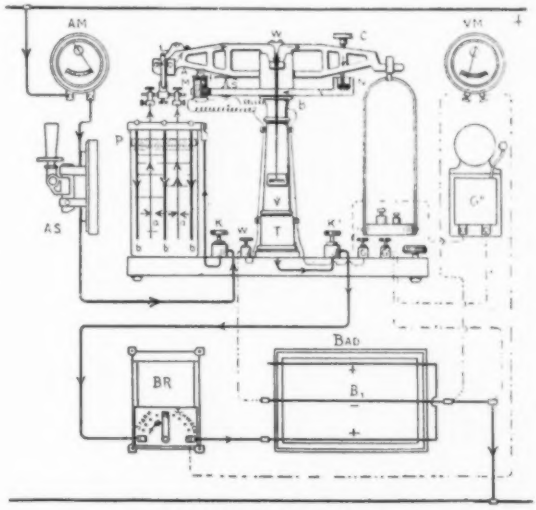
tery cells is conducted through the apparatus, and the time is noted when hydrogen begins to appear at the negative pole. The position of the liquid in the measuring tubes is then read off, the height of the liquid in the funnel tube above the level in the measuring tubes is measured with a millimeter scale, and the current is sent through the apparatus for a measured time. Then the gas volumes are read off, the differences of the levels between the funnel tube and the measuring tubes are read, the gas volumes are reduced to equal pressures, and the depolarising effect of the manganese peroxide body is calculated from the deficiency of hydrogen.

Accumulator "Max."—L'Elettricista, of August 1, contains a description of the accumulator "Max," which is stated to have been tried, with favorable results, by the French navy department. It consists of a number of electrodes, each of which has a central core of rolled antimonial lead wire, which is surrounded by a layer of active material about 3 mm. thick. The active mass is brought upon the electrodes under considerable pressure. A table gives the principal characteristics of the accumulator.

Conversion of Persulphuric Acid into Caro Acid.—In the course of experiments on the phenomena which take place in the charging of storage batteries, Mugdan endeavored to find an answer to the question whether in the electrolysis of sulphuric acid there are formed at a platinum anode other oxidising bodies in appreciable quantity besides the primarily-formed persulphuric acid and the caro acid which is formed from the latter. The caro acid can be determined by its oxidising action on KI, while the total amount of both acids can be determined by their oxydising action on Fe SO_4. The above question was sought to be solved by measuring the speed of conversion of one acid into the other, in order to find out whether a speed-constant could be found. The establishment of such a constant would at least make it probable that only these two oxidising bodies appear in the anode compartment, when sulphuric acid is electrolysed. The author found in the anode compartment of fresh acid, electrolysed with good cooling, only traces of the substance acting on KI; this is, therefore, only formed secondarily. With regard to this, an exact constancy of the speed coefficient would prove that primarily only one oxidising substance, namely, persulphuric acid, is formed, because in the other case a proportionality between the quantity changing in the unit of time to the quantity present would not appear. The expression for the monomolecular reaction was found nearly constant, but the measurements could not be carried out with sufficient exactness to draw the above conclusion. The experiments were carried out by electrolysing sulphuric acid of about 40 per cent, with varying current densities of 2 amperes to 4 amperes per sq. cm The electrolyte was cooled, and a diaphragm previously extracted with acid was employed. The time of electrolysis was about two hours. The anodic liquid, after dilution, was brought into a thermostat of 25°, and samples taken from time to time and titrated. The caro acid was determined in a sample taken at the same time, after strongly diluting it with ice water, and adding KI, by titration with thiosulphate without the use of starch. The experiments were always carried out with a great excess of acid, so that the change of acidity due to the reaction could be neglected. The second part of the article, in the *Zeitsch. f. Electrochem.*, August 27, in which the author gives the results of his experiments, is devoted to an investigation to establish the formula of the caro acid. The formula has been given as $H_2S_2O_5$ and H_2SO_5. The reaction between caro acid and KI is either: $H_2SO_5 + 2KI = K_2SO_4 + 2I + H_2O$; or $H_2S_2O_5 + 4KI = 2K_2SO_4 + 4I + H_2O$. In the first case the relation of the liberated iodine to the decrease of acidity is as 1 to 1, in the second case as 2 to 1. The author found in a series of experiments the relation nearly as 2 to 1, and considers, therefore, the formula $H_2S_2O_5$ as the most probable.

General and Miscellaneous.

Voltametric Balance.—The voltametric balance of Dr. Pfanhauser serves to determine the weight of electrolytic metal deposits during the process of electroplating. The instrument acts thus as an ampere hour meter, and the thickness of the metallic deposit can be very closely regulated, as the process is automatically interrupted when the desired thickness of the deposit is obtained. Several improvements, in the form of the balance, as described previously, are given by the inventor in *Zeitsch. f. Electrochem.*, August 13. The general arrangement of the balance is shown in the figure below. The improvement consists in the arrangement of an electromagnet *M*, below an iron contact *A* on the beam of the balance. A spring *F* is also situated on the beam, which, when the cathodes *a* of the voltameter *P* have received their predetermined weight of deposit, touches a contact *S*. By this means a shunt current is closed, which energizes the magnet *M*. This attracts then the pole piece *a* in the beam of the balance, with the result that the beam is quickly pulled down, and the contact between a set screw *C* and a layer of mercury *N* on the other arm of the balance, is broken abruptly. The breaking of this contact interrupts the circuit of the plating



VOLTAMETRIC BALANCE.

bath. By this means it is made possible to interrupt the plating current at the exact time the predetermined amount of deposit is obtained, while with the former arrangement, when the set screw and the mercury vessel only were depended upon to break the bath circuit, errors of 5 per cent to 6 per cent of the total weight of the deposit occurred, as the break did not take place with sufficient accuracy. At the same time that the bath circuit is broken, a bell G″ rings to advise the attendant. The manipulation and regulation of the balance is described in detail.

Dryers and Drying Out for Electroplating Purposes.—Under this title F. P. Davis, in *Metal Industry*, August, gives the results of his observations and experiences on the proper construction of drying apparatus for drying materials, which have been electroplated. He illustrates and describes in detail the arrangement of such an apparatus. Attention is drawn to the fact that too little consideration is usually given to the sawdust that is used for drying out, and the author discusses that question. According to him, for brass work after acid dipping, nickel work to be buffed, and the coarser grades of plated work, whitewood sawdust is very good. The sawdust should be from well seasoned lumber. "Gray" or "white" nickeled work, as it is variously designated, that is, work that is acid dipped or polished by attrition in a tumbling barrel, and plated with no further finish, is stated

to require much care in drying to retain its clear, light color. The essential point is said to be often overlooked, namely, that the work should be taken from the cold rinsing water directly to the dryer, and in no case should hot rinsing water be added, as the latter will invariably darken the work and turn it yellow. The dryer must be hot, and the work stirred about and agitated until dry, and then immediately removed, as any unnecessary heating will cause discoloration. The author states that small brass-plated articles and goods that are coppered merely to give color, and that are to be lacquered, with no further finish after plating, should always be dried without the use of hot water. The drying of plated work which is to be buffed after plating, will be greatly facilitated by rinsing a few seconds in hot, soapy water, and then passing it through clean, hot water. The brilliancy of articles which have been plated with just enough silver to whiten them is stated to be greatly increased if this process is used. The author thinks that it is small matters of detail like these that are worthy of attention, inasmuch as they help towards perfect work.

Soldering of Aluminium to Steel and Iron.—A note from the *Oester. Zeitsch. f. Berg. u. Huettenwesen*, reprinted in *Chemische Zeitschrift*, September 1, on a new method for the above purpose. The method consists mainly in covering the iron pieces electrolytically with a layer of copper, and then pouring aluminium on them, which unites homogeneously with the copper. In this manner tubes or cylinders of cast iron, steel or wrought iron can be made with aluminium bosses. The iron parts which are to be treated are cleaned with caustic potash, and then connected as cathodes in an electrolytic vessel, filled with acidified ammonium oxalate solution; the anodes are sheets of copper. After a thin layer of copper has been deposited on the material, it is taken out and brought into an ordinary acid galvanoplastic bath, made up with copper sulphate and sulphuric acid, where it stays until the desired thickness of the copper is obtained. The material is then dried in an atmosphere as little oxidising as possible, and put into a suitable mold, into which the aluminium, heated to a cherry-red temperature, is poured. On account of the great affinity between copper and aluminium the metals unite readily, and the soldering is stated to be effected in a most satisfactory manner.

Thermochemistry in 1902 to the Middle of 1903.—In the *Chemische Zeitschrift*, September 1, Prof Cohen gives a short review of the work done in this field during the above time. Among others, he refers to the work of T. W. Richards, who showed that the thermochemical data, as given usually, contain certain errors, due to the neglect of the fact that the specific heats of reacting systems are changing during the reaction, and advocated the recalculation of all thermochemical data for a predetermined temperature (as, for instance, 20°), and to use the exact atomic weight numbers for O = 16.

Physico-Chemical Institute of the University of Freiburg.—*The Zeitsch. f. Electrochem.* June 11, contains the description of the new institute, by the director, Dr. G. Meyer. Current for electrochemical purposes is furnished by the street current of 2 x 220 volts. Two storage batteries are provided, one of 144, and another of 12 cells. The first battery is charged directly from the street mains with 440 volts, and is discharged in four or eight groups in parallel, with 72 or 36 volts. It has such capacity, that with one hour discharge at these voltages, currents of 300 or 600 amperes can be furnished. Lines for 50 amperes maximum run to the laboratory rooms, and 300 amperes maximum to the lecture room. A room for high-temperature electrochemical experiments is situated close to the battery, in which current up to 600 amperes can be obtained. With the help of the batteries, potentials of 72, 36, 24 and 8 volts are available, also 220 volts everywhere from the lighting circuit, and at three places provision is made for taking off 440 volts. A short description is given of the outfit for the electrochemical laboratory and for the lecture room.

ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

By George P. Scholl, Ph. D.

Electric Furnaces and Furnace Products.

Electric Furnace or Oven. A. Eimer, New York. Patent 736,509, August 18, 1903. Application filed May 22, 1903.

The invention relates to a furnace in which small articles, as artificial teeth, chemists' crucibles, etc., may be heated. The furnace is constructed in a shape similar to that of a muffle, and the heating is accomplished by a resistance conductor, f. i. platinum wire. The heating member of the furnace is represented by a plate of refractory material, provided on its upper surface with a series of grooves or channels, in which the conductor is placed, and adapted to slide within the furnace upon the base-plate. Provision is also made for heating the upper part of the furnace. Various modifications in the disposition of the current-carrying conductor within the base-plate are also described.

Electric Sectional Furnace. August Eimer, New York. Patent 736,917, August 18, 1903. Application filed May 28, 1903.

The specification describes a furnace of the resistance-heating type, primarily intended for laboratory purposes. The furnace consists essentially of a trough-shaped receptacle of refractory material, which forms the bottom and the side walls. The roof of the furnace is represented by an independent cover of refractory material provided with observation apertures. The furnace is built up of a series of independent sections, and the connections are so arranged that either of the sections can be used by itself, or they may be connected in series, or in multiple. The heating is accomplished by radiation from a resistance conductor, which is embedded within the walls of the furnace, near its inner surface. Suitable provision is made to prevent loss of heat by radiation, and the connections are so arranged that the changes in the connections can be carried out quickly and conveniently.

Apparatus for the Electrolysis of Fused Substances. C. W. Roepper, Philadelphia. Patent 736,020, August 11, 1903. Application filed September 27, 1898.

The specification describes and illustrates several constructive forms of apparatus for the electrolysis of fused substances, which are designed primarily with a view of providing means for easily accomplishing the removal and renewal of that part of the apparatus, which is exposed to the action of the heating flame, where the apparatus is heated externally. In the constructions shown heat is applied to the bottom of the apparatus and the latter is constructed of a plate of various forms, suitable for particular purposes, which is made entirely independent of the rest of the furnace. The joint between this bottom plate and the furnace walls is kept tight by a cooling arrangement. When this bottom plate burns through, or shows signs of weakness, it can easily be removed and another one substituted for it.

Process of Producing Chlorides of Carbon. F. J. Machalske, Chicago. Patent 737,123, August 25, 1903. Application filed September 24, 1902.

The process consists in introducing a mixture of dry broken

coke, sodium chloride and pure silica sand into an electric furnace, consisting of a stack of firebrick with a magnesia lining, 2 carbon electrodes being introduced adjustably through the sides. An outlet flue for the chlorides of carbon is provided at the top, and a tap-hole is arranged at the bottom. The charge surrounds the electrodes, and the electric current passing between the latter heats it to a temperature sufficient to effect the reaction. The charge employed differs entirely from that used for the production of silicon carbide, where a small amount of sodium chloride is also usually added as a flux, in as much as the chlorine compound is used in much larger proportions. The temperature required is also lower than that necessary for the production of silicon carbide, as it is below 2000° C. The inventor states that it is probable, that at the high temperature the sodium chloride is first melted, and that the silica then reacts with the molten chloride to liberate chlorine, which in its turn combines with the incandescent coke to produce the chloride of carbon. The resulting chloride passes through a reflux condenser and the molten residue is drawn off through the tapping hole. Various chlorides of carbon may be produced by varying the proportions of the constituents of the charge, a typical reaction being $6NaCl + 2SiO_2 + 4C = C_2Cl_4 + C_2Cl_2 + [Si(ONa)_4 + Na_2Si]$. Sulphur chloride may be produced simultaneously with the carbon chlorides by adding sulphur to the charge, the reaction proceeding according to the equation, $6NaCl + 2SiO_2 + C + 2S = CCl_4 + S_2Cl_2 + [Si(ONa)_4 + Na_2Si]$.

APPARATUS AND PROCESSES FOR THE ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

Electrolytic Apparatus. L. P. Burrows, Washington, D. C. Patent 737,554, August 25, 1903. Application filed January 22, 1902.

This apparatus is especially intended for the treatment of ores. It consists of a series of vessels arranged in cascade form, the upper one of which acts as a receiving and dissolving vessel for the ore. From there the latter passes into one of a series of filtering vessels, and thence into a receiving trough, which delivers it to the vessels in which the electrolysis of the solution obtained from the ore takes place. The ore is fed in a continuous stream into the receiving vessel, which is provided with a stirrer of peculiar construction, so arranged that the ore and any solvent which may be introduced into the vessel are brought into intimate contact. The stirrer is connected to the positive terminal of a source of electricity of a suitably high voltage, as, for instance, a dynamo of 110 volts. The ore pulp which is fed into the vessel, preferably contains sodium chloride or another electrolyte capable of furnishing a solvent anion. The oxygen and the chlorine liberated on the surfaces of the stirrer are stated to effect the rapid solution of any metal values contained in the ore pulp. The solution and the undissolved particles of the ore then pass in a full stream into one of the filtering vessels, and this stream serves as a path for the current from the solution in the dissolving vessel to that in the filter. Similarly the outlet stream from the filtering vessel carries the current into the receiving trough, and a stream from this trough carries it into the vessel in which deposition takes place. This vessel contains a ring-shaped cathode, which is connected with the negative terminal of the source of electricity. Wires also lead from one vessel to the other to act as safeguards and prevent interruption of the current in case the liquid connection should be broken. These wires are preferably insulated, except at their ends, which are in electrical contact with any solution remaining in the lower part of each vessel. The inventor states that the electric current not only serves to effect solution of the metals in the dissolving vessel and redeposition of these metals upon the cathodes, but also keeps all portions of the solution, whether in the several vessels or flowing through the connecting pipes and hoses, at a high temperature. The inventor does not disclose of what material this anodic stirrer is made, beyond saying that it is of metal. It would be interesting to know what material he has found to resist the action of the chlorine under these circumstances.

Electrolytic Apparatus. G. Bell and G. W. Bell, of Liverpool, England. Patent 737,566, September 1, 1903. Application filed June 18, 1901.

The apparatus described in the specification is primarily intended for the electrolysis of sodium chloride for the production of caustic soda and chlorine, and belongs to the mercury type of apparatus. The distinctive feature of the apparatus is contained in the fact that the transference of the sodium mercury amalgam from the compartment where it is charged into the compartment where it is to be discharged, is effected by means of the pressure exerted by the hydrogen, which is evolved in the discharge compartment. The apparatus is shown in cross-section in Fig. 1. In appearance it is much like a Castner apparatus, with its middle comparment *a*, however, serving as electrolytic compartment, while the discharge of the amalgam takes place in the two outer compartments *b*. The bottom of the middle compartment is raised above that of the outer compartments, and is so constructed that there is always a layer of mercury remaining on the bottom of the compartment in order not to interrupt the current. The move-

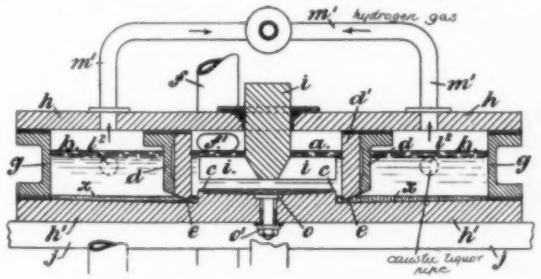


FIG. 1.—BELL MERCURY CATHODE BELL.

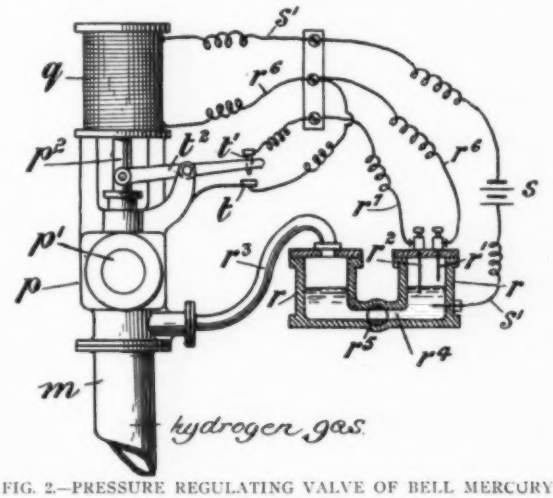


FIG. 2.—PRESSURE REGULATING VALVE OF BELL MERCURY CATHODE BELL.

ment of the mercury to and from the electrolytic and discharge compartments is controlled by a valve on the upper end of the main hydrogen pipe *m*. When this valve is closed, the hydrogen generated by the discharge of the amalgam in the compartments *b* accumulates and its pressure gradually rises, until it has reached such height that it forces the mercury *x* from the bottom of the compartments through the passage *e* into the electrolytic compartment. While there, it receives a fresh charge of sodium, and after it is sufficiently charged the valve is opened, the pressure falls, and the amalgam flows by gravity into the discharge compartments, where

the same cycle of operations is repeated again. The anode *i* consists of a vertical trunk, passing through the cover *h* and having horizontal bars projecting on either side from its lower end. The connection with the negative terminal of the current is made by a cathode plate *o* introduced into the electrolytic compartment through the bottom; f^1 is a pipe which serves to carry away the chlorine. The pressure regulating valve is actuated by a peculiar device, which is illustrated in Fig. 2. It consists of an electromagnet *g*, which acts directly on the spindle p_2 of the valve p_1 and a contact device consisting of a chamber *r*, containing mercury and provided with contact points r^1, r^2. Chamber r is in communication with the hydrogen pipe *m* through a passage r^3, and is connected with the pressure chamber by means of a conduit r^4, the area of which is controlled by the cock r^5. As the pressure of the hydrogen rises in the discharge compartment *b*, the mercury in the chamber *r* is forced upwards until it comes in contact with the contacts r^2. The circuit connected with this terminal, however, is open, and the magnet *g* is not energized, until the mercury reaches the contact point r_1. The valve rod p^2 is then pulled up and the valve opened, whereupon the mercury begins to fall down again, the valve, however, not being closed until it reaches the contact point r^3. The time taken in the performance of a complete cycle of operations will depend upon the differences of level of the two terminals of the valve-controlling device, and on the velocity of rise and fall of the mercury, which latter can be regulated by adjusting the opening through which the mercury passes and the relative height of the contact points.

Cathode for Electric Detinning Baths. M. Larnoes and J. Dunn, Streator, Ill. Patent 737,423, August 25, 1903. Application filed November 25, 1902.

This invention relates to an improved form of cathode, which is made of a plate of sheet-iron or steel and riveted to a transverse suspension rod, in order that there should be no obstruction to the scraping tool when the tin deposited on the cathode is removed. The plate is also provided with a hand-hole, so that it can be handled with great facility.

Connecting Hook for Electrotypers. J. W. Cornelius and J. Niemer, Cincinnati, Ohio. Patent 737,353, August 25, 1903. Application filed July 5, 1902.

The inventor describes two forms of hooks used by electrotypers for suspending cathode or anode plates into the plating solution. The hooks serve at the same time as conductors of the current, and are so constructed that the plates can be entirely submerged in the electroplating solution. The upper part of the hook consists of copper, while the lower part, in which the plates are held, is composed of lead, or a combination of lead, tin and antimony. The mechanical construction is described at length.

Process of Zincing Objects by Electrolysis. S. Szirmay, Budapest, Austria-Hungary. Patent 736,565, August 18, 1903. Application filed November 12, 1900.

The inventor proposes to overcome all the disadvantages in the commercial deposition of zinc by electrolysis, which he discusses at considerable length, by adding to an electrolyte consisting of sulphate of zinc, a certain amount of dextrose and of the mixed sulphates of aluminium and magnesium. The electrolyte is made up by first dissolving 13 kg. of sulphate of zinc per 100 liters of warm water. A mixture of 1 kg. in definite proportions of sulphate of aluminium and sulphate of magnesium, and 3 kg. of dextrose are dissolved separately in boiling water, allowed to cool and mixed together, after which the resultant solution is added to the zinc sulphate solution. Pure rolled zinc is used as anode, and the electrodeposition is carried out at a temperature of about 18° C., with a current of about 100 amperes per square meter of cathode surface, and 4 to 4½ volts. The electrolyte is maintained at its original concentration by adding periodically fifteen cc. of the solution of dextrose and the mixed sulphates per square meter of cathode surface.

Electrolytic Decomposition of Saline Solutions. A. B. Larchar, Oldtown, Me. Patent 736,982, August 25, 1903. Application filed October 9, 1900.

The specification describes an apparatus for the electrolysis of sodium chloride solutions of the diaphragm type. The cathode of this apparatus is of peculiar construction, consisting of sections of a soft steel grating, which form the four side walls of the inner compartment and serve to support the diaphragm which is stretched upon their inner side, and also the cover of the cell, from which the anodes are suspended. The cathode grating consists of a series of bars or slats, oblong in cross-section and ¾ inch wide by 0.049 inch thick, disposed at right angles to the plane of the wall, of which they form a part. The slats are spaced uniformly apart, and passages or channels are thus formed, leading outward from the diaphragm. In this way there is formed a lamellar cathode, which acts to divide the liquid into a great number of films, which pass from the diaphragm outwards through the cathode into the tank, which surrounds the whole construction. The diaphragm consists preferably of three or four thicknesses of asbestos paper, and the anodes are a series of graphitized carbon slabs, each inclined from top to bottom towards the diaphragm wall adjacent to it. Arrangements for drawing off the caustic soda solution and maintaining the rate of percolation are described in detail. The inventor states that he worked with an apparatus containing fourteen hundred slats of the dimensions given above, twenty-two anodes, each 1¼ inches by 4 inches in cross-section, and 20 square feet of diaphragm composed of three plies of asbestos paper, each 1-32 inch thick. The height of the cell was about 30 inches, and the depth of the brine about 24 inches. Six hundred amperes were used at a voltage of 3.8. The best results were secured by maintaining the level of the liquid inside the cell about 1½ inches above the liquid outside of the cell.

Method of Recovering Tin from Scraps of Tinned Iron. B. A. Bergman, Nyfors, Sweden. Patent 736,924, August 25, 1903. Application filed January 15, 1902.

The inventor claims to overcome all difficulties in the recovery of tin from scraps by the use of a depolarizing compound in the vessel in which the tin is dissolved from the scrap. He arranges an iron tank filled with a solution of caustic, into which is suspended a basket containing the tin scraps and resting on insulating blocks. On the bottom of the vessel there is a layer of oxide of copper, which is to play the role of a depolarizer. The arrangement is supposed to act as a battery and to charge a storage battery, whichi is to serve the purpose of furnishing current for the subsequent deposition of the tin from the alkali stannate solution obtained in the cell.

Reduction of Nitro and Azo Compounds. M. Buchner, Mannheim, Germany, assignor to C. F. Boehringer and Soehne. Patent 736,204, August 11, 1903. Application filed September 24, 1900.

The inventor states that he has found that tin may be precipitated even from strong acid solutions of tin in hydrochloric acid, which remain after the reduction of nitro or azo compounds, if the reducing process is so conducted that the tin employed is converted into stannous chloride only. Under these conditions there is no loss in current efficiency, as is the case when stannic chloride is employed, and even high current densities can be used. The reduction of para-amido-azo-benzol chloride is described as follows: 2.334 kg. of amido-azo-benzol chloride are intimately mixed with 2.66 kg. of electrolytically precipitated powdered tin. Five kilograms of water are then added, and the whole is well mixed, whereupon 4.5 liters of fuming hydrochloric acid are gradually added. After the reduction due to this mixture has been completed, the reduction bath is maintained in a heated condition for several hours, and then allowed to cool and drain from the excess of tin. The reduction solution is then poured into the cathode space of an electrolytic cell provided with a diaphragm. Any indifferent metal may serve as cathode and anode. The current density is about

1800 amperes (evidently per square meter). Towards the end of electrolysis, when the concentration of the tin ions decreases considerably, it is advantageous to reduce this current density. Thus, 2.5 kg. of tin are recovered from 2.66 kg. originally employed. The mother liquor may then be saturated with HCl gas in the cold and the chloride of paraphenyldiamine thus precipitated. The cooling of the cathode compartment is effected by a cooling coil arranged therein.

Reduction of Nitro Compounds. M. Buchner, Mannheim, Germany, assignor to Boehringer and Soehne. Patent 736,205, August 11, 1903. Application filed September 24, 1900.

The invention relates to the reduction of nitro compounds in the presence of lead, mercury, chromium or iron ions. The reduction of nitrobenzene by the addition of lead chloride to the cathode electrolyte is carried out in an apparatus provided with a diaphragm. The anode electrolyte consists of a 10 per cent solution of sulphuric acid, any suitable indifferent metal being used as anode. The cathode compartment contains a cylindrical platinum electrode, and a mixture of 500 parts by weight of fuming HCl, 500 parts by weight of water, 125 parts by weight of nitrobenzene and 50 parts, by weight, of lead chloride. The nitrobenzene is kept in suspension by constantly stirring the liquid, and is replaced by a fresh supply when it is consumed. During electrolysis the mixture is preferably cooled. The current has a density of about 1900 amperes per square meter, and is maintained until regular liberation of H takes place and becomes visible. After electrolysis is completed, the lead will be found in the form of fine metallic sponge, and none will be found in the cathode electrolyte. Instead of the fifty parts of lead chloride, forty parts of finely divided metallic lead may be added to the cathode electrolyte, and the process carried out in substantially the same manner. The conditions and proportions are also the same as above when ferrous chloride is added to the cathode electrolyte, but in this case only ferrous chloride, no metallic iron, is regenerated.

Reduction of Aromatic Nitro-Compounds. Max Buchner. Mannheim, Germany, assignor to Boehringer and Soehne. Patent 736,206, August 11, 1903. Application filed December 14, 1901.

The inventor has discovered that nitro bodies dissolved or suspended in an alkaline bath containing a salt, oxide, or other compound of an alkali, may be reduced to the corresponding amines, if a cathode, preferably of copper, is employed, together with powdered copper. The reduction of nitrobenzene to aniline is described as follows: A concentrated solution of sodium chloride is introduced into the anode compartment of a diaphragm cell which contains a carbon anode. The cathode chamber is provided with cooling and stirring devices. The solution in the cathode compartment consists of 1440 parts by weight of a concentrated sodium chloride solution, 50 to 100 parts by weight of powdered copper, and 123 parts by weight of nitrobenzene. The cathode is of metallic copper and the reduction is carried out, preferably with a current density of about 1500 amperes per square meter, and at 80° to 100° C. The voltage will, under these conditions, amount to about 5 volts. The process is discontinued after the amount of current calculated for the complete reduction to aniline has passed through. Examples are also given for the reduction of nitrobenzene to aniline with a copper cathode in alcoholic solution, with a barium chloride bath, with a platinum cathode in the presence of powdered copper, with a tin cathode in the presence of powdered copper, with a copper cathode in the presence of cuprous chloride, and with a nickel cathode in the presence of copper sulphate. The reduction of orthonitrotoluene to orthotoluidene, of meta-nitraniline to meta-phenylene-diamine, and of alpha-nitronaphtalene to alpha-naphtylamine is also described.

Apparatus for Electroplating Small Metallic Articles. J. F. Shelton, Fort Worth, Texas. Patent 737,162, August 25, 1903. Application filed September 16, 1901.

The specification describes in detail a mechanical construction, the main part of which consists of a perforated wooden cylinder, mounted on a wooden shaft, around which is wound a conductor in communication at its ends, with the negative terminals of a source of electricity. The positive terminal is connected to a series of rods, from which the anodes are suspended. The wooden cylinder is filled with the small articles to be plated, which are thus constituted cathodes. The cylinder is rotated during the operation of plating by a belt running on its surface.

Primary Batteries.

Portable Electric Accumulator. L. A. Lammerts, Rotterdam, Netherlands. Patent 734,896, July 28, 1903. Application filed June 20, 1902.

The invention relates to portable electric accumulators, which are carried by the user in the pocket or are fixed to bicycles, etc. The object of the invention is to secure the conductors between the electrodes and pole terminals as effectively as possible from oxidation. The inventor claims that straight wires from the electrodes, passing through a layer of non-conducting material on their way to the battery terminals, are liable to rapid destruction, as the joint with the enclosing material is not sufficiently tight to prevent moisture from the electrolyte or the moist gases and vapors from penetrating to them and attacking them. He claims that a good protection can be secured by constructing the connecting wires in the shape of cylindrically coiled helical springs, as this shape has proved to permit the insulating material cast above the cells to adhere to and tightly surround the wires on all points.

Dry Battery. E. M. Fishell and M. H. Moffett, Cleveland, Ohio. Patent 733,178, July 7, 1903. Application filed April 14, 1902

The object is to provide a dry battery composed of a plurality of cells which are compactly and immovably enclosed in a case impervious to moisture and especially constructed to permit rough handling. The cell is primarily intended for use on automobiles and launches. The cells themselves are of the well-known form of dry batteries, with an outer cup of zinc, serving at the same time as electrode, and as the containing vessel. There are four cells of this kind arranged in a case, preferably made of tin, with semi-circular ends and flat sides. Provisions are made to maintain the cells and the terminals of the battery in their proper position.

Galvanic Battery. E. L. Anderson, St. Louis. Patent 732,811, July 7, 1903. Application filed July 9, 1902.

The object is to construct a galvanic battery of the zinc carbon type, the carbon electrode of which is provided with a depolarizing material, which battery shall be simple of construction and so arranged that the depolarizer can be easily renewed. The inventor uses a round hollow carbon electrode, placed in the jar which contains the electrolyte. The hollow chamber in the interior of the electrode is intended to receive the charge of depolarizer. A cylindrical zinc electrode surrounds the carbon. A removable bottom of porcelain holds the depolarizer in place in the hollow carbon electrode, which latter is of such a shape that it serves at the same time as cover for the containing jar. The electrodes can be easily removed for cleaning purposes or for renewal of the depolarizer.

Battery. D. Drawbough, Eberlys Mill, Pa. Patent 733,949, July 21, 1903. Application filed April 12, 1902.

The battery belongs to the class of dry batteries of the zinc carbon type. The outer cylinder of zinc constitutes one of the electrodes. The other electrode is formed of a flat stick of carbon, arranged in the center of the zinc cylinder. This carbon is surrounded by a composition of coke, plumbago and a small quantity of plaster of paris, so as to form a paste. Around this composition is placed a cylinder of paper

or other porous material which forms a partition between the composition and the electrolyte proper. The latter consists of concentrated caustic soda, with a small amount of alkali to hold it in place. The cell is hermetically sealed in the usual manner. Cheapness of construction is one of the advantages claimed for this battery.

Galvanic Battery. D. L. Winters, Chicago. Patent 734,646, July 28, 1903. Application filed May 27, 1903.

The object is to provide a battery to be used for operating spark coils of explosive engines, and similar applications. It is constructed in such a manner that the number of individual cells can be increased or decreased easily, without interrupting the current. The object is attained by constructing the electrodes in a peculiar manner, and providing long-yielding terminals or contact fingers, which press against the electrodes. When the latter are removed the contact fingers press against each other, thus forming a metallic connection.

Electric Battery. Henry Csanyi, Felsoe-Dobsza, Austria-Hungary. Patent 734,826, July 28, 1903. Application filed March 4, 1903.

The invention relates to a battery of the zinc carbon type, with a porous partition separating the electrodes. The carbon electrode is immersed in nitric acid of 40° to 50° B., and the zinc in an alcoholic solution of 5° to 15° B. of pernitrate of mercury and potassium cyanide. The inventor gives as an example of a suitable composition for the alcoholic solution the following: 1000 grms of 25 per cent alcohol, 150 grams of 48 per cent nitric acid, 10 grams of oxide of mercury, and six grams of potassium cyanide solution of 60 per cent. The partition may be formed of a mixture of clay and pieces of carbon, which latter have been burned by heating the mixture.

Galvanic Battery. H. Halsey, New York. Patent 734,546, July 28, 1903. Application filed Dec. 10, 1901.

The specification describes another arrangement embodying the inventor's idea as shown in former patents, of rotating one or both electrodes of a galvanic cell. Means are described in detail, whereby the carbon electrode of a zinc carbon cell is rotated by means of a small electric motor, driven by the cell itself.

Electric Battery. H. Halsey, New York. Patent 734,547, July 28, 1903. Application filed April 18, 1902.

In this arrangement the idea of the inventor has been to obtain the advantages derived by the use of a movable element without moving the element itself. Means are therefore provided to rotate the receptacle containing the electrolyte.

Electric Battery. H. Halsey, New York. Patent 734,548, July 28, 1903. Application filed April 18, 1902.

The object to provide a battery with movable elements, in which all the parts are to be simple and readily fitted together, and where the interior of the battery is readily accessible. The carbon element is hung upon a spider and revolves. The construction is described in detail.

Electric Battery. H. Halsey, New York. Patent 734,549, July 28, 1903. Application filed April 18, 1902.

The arrangement of this battery is such that the movement of the electrolyte is effected by one or more propellers, the movable shaft being either brought in through the bottom or the cover of the cell. A small motor driven by the battery itself again furnishes the motive power.

Electric Battery. H. Halsey, New York. Patent 734,857, July 28, 1903. Application filed April 18, 1902.

In this battery a series of stirrers are arranged which brush the electrodes of the element. They are carried on a shaft on top of the battery, and receive an oscillating motion by means of a cam situated on the motor shaft, which cam strikes and operates the end of a lever connected to the stirrers.

Electric Battery. H. Halsey, New York. Patent 734,858, July 28, 1903. Application filed August 2, 1902.

In this construction the movable shaft enters through the bottom of the vessel containing the electrolyte, and carries the carbon element of the battery, which, however, is not in direct contact with the electrolyte proper, but is surrounded by the depolarizer.

Storage Batteries.

Reversible Galvanic Battery. E. W. Jungner, Norrkoeping, Sweden. Patent 738,110, September 1, 1903. Application filed April 17, 1899. Divided and filed again June 23, 1902.

The cell described in the specification works with an alkaline electrolyte, which is not changed during charge and discharge, but merely serves as an oxygen carrier from one electrode to the other. The positive electrode is made up of a mixture of hydrated peroxide of manganese and graphite, moistened with water, and is introduced between two perforated nickel plates, which have been connected in a suitable manner, and then subjected to pressure. The negative electrode is made in a similar manner, but the active mass consists of a mixture of ferric hydrate and graphite. The ferric hydrate has been partly reduced to ferrous hydrate and metallic iron by cathode electrolysis in an alkaline solution. Perforated plates of copper are used as carriers in this case. The electrodes are placed alternately in the cell and separated by a porous or perforated insulating material. When the cell is discharged the following reactions take place: 1. $Fe + KOH + 2Mn(OH)_4 = Fe(OH)_2 + KOH + 2Mn(OH)_3$. 2. $Fe(OH)_2 + KOH + Mn(OH)_4 = Fe(OH)_3 + KOH + Mn(OH)_3$. The reaction 1, which takes place only when the charging has been carried so far as to produce metallic iron, gives a voltage of 0.8 volt, and reaction 2 a voltage of 0.6 volt.

Secondary Battery. G. E. Hatch, Quincy, Mass. Patent 736,390, August 18, 1903. Application filed July 14, 1899.

The positive electrode of this battery is made up of red lead in the form of a paste, which is introduced into the parallel grooves of two rigid porous support plates, made of kaolin or a similar acid-resisting material containing no iron. A thin lead plate in the middle serves as conductor, but does not perform any supporting function of the action mass, which latter is held altogether by the porous plates. The thin conducting plate may be perforated and the holes thus formed filled with acid intended to act as a reservoir when the battery discharge is unusually high. The negative plates are formed by filling the active material into a shallow perforated wooden mold and reducing it by a forming process to metallic lead. A conducting plate of thin lead has been introduced into the active material before the forming takes place. It is claimed that by the forming process the plate is brought into the condition of a firm, coherent plate of porous or spongy metallic lead, which is self-supporting. In assembling the cell, the grooves of the above porous plates are preferably placed in a vertical position, in order to provide a free passage upwards for the gases.

Secondary Battery. J. Middleby, Malden, Mass. Patent 736,420, August 18, 1903. Application filed November 22, 1899.

The invention is intended to provide a storage battery in which negative electrodes of zinc may be used with positive plates of lead. The electrolyte used by preference is composed of a solution of pure water, to which is added, in the order named, about one-twentieth of its volume of chemically pure sulphuric acid, sulphate of mercury slightly in excess of what will be dissolved by the hot mixture, and carbonate of ammonia in the proportion of from two to four ounces to each gallon of the mixed water and acid Each zinc electrode is confined between two porous plates, the edges of which are raised on all sides, except the top side, so that they form a containing vessel when put face to face. The positive plates are formed of active lead material in the usual manner.

We have received from the Westinghouse Electric & Manufacturing Co. their circulars, 1044 for direct-connected railway generators and 1048 for railway motors.

INTERNATIONAL CONGRESS FOR APPLIED CHEMISTRY.

Report of the Proceedings of Section X.
(Electrochemistry and Physical Chemistry.)

By H. Danneel, Ph. D., and J. K. Clement.

(Continued from page 462.)

Meeting on June 4, Afternoon.

The Composition of Electrometallurgic Products Containing Silicon.

A paper on this subject was presented by P. Lebeau, of Paris. By melting together copper silicide and cobalt, the author obtained a compound having the formula Si Co. In iron silicides which contain 10 to 20 per cent Si the definite compounds SiFe and $SiFe_2$ exist and the silicide Fe Si_2 has also been prepared. A series of other compounds were also obtained by melting together metals with copper silicide. The metals Ag, Sn, Zn, Al form alloys with the copper and the silicon is obtained in the form of small crystals distributed through the mass. Other metals, however, act upon copper silicide, in that they take away the silicon from the latter and form other silicides. By dissolving the copper in nitric acid, which does not act upon the silicides, these can be easily isolated. The following silicides have been obtained:

Fe_2 Si	Co_2 Si	Mn_2 Si	Cr_3 Si
Fe Si	Co Si	Mn Si	Cr_2 Si
Fe Si_2	Co Si_2	Mn Si_2	Cr_3 Si_2
			Cr Si_2

Nickel silicide was also obtained, but its isolation is difficult, owing to the fact that it is attacked by nitric acid. A thorough study of the ferrosilicides led to the conclusion that in the technical product the silicon is always in the form of Fe_2 Si. There was no discussion.

The Specific Action of Metals in Electrolytic Reduction and Oxidation.

In a paper on this subject A. Coehn gave a comprehensive summary of the reducing action of different metals, especially upon organic bodies; and he traced the various "reduction potentials" back to Caspari's theory of overvoltage (Ueberspannung). According to this, different cathode potentials are required for producing hydrogen at cathodes of different metals.

It was next shown that this was no peculiar property of hydrogen alone, but that oxygen behaves similarly. In the case of the latter a lively evolution of oxygen gas takes places on bright platinum at 1.67 volts, on copper oxide at 1.48 volts, on nickel at 1.35 volts, and at spongy nickel even at 1.28 volts. With this phenomenon of overvoltage it is possible to explain a long series of chemical phenomena, which, up to the present were inexplicable.

A new example is offered in the case of Marsh's test for arsenic. While the addition of platinum sets up a more violent evolution of hydrogen, yet the hydrogen is not evolved with a potential sufficiently high to form arsenuretted hydrogen. If only zinc is present then the potential is sufficient. Coehn then spoke of the work of various investigators upon the electrolytic reduction of organic bodies; also on the oxidation of chromium salts, and on the electrolytic oxidation of p. nitrotoluol to p. nitrobenzoic acid which was formerly impossible, but which can now be carried out by making use of the overvoltage of oxygen on a PbO_2 anode.

In addition to the phenomena due to overvoltage, others depend upon the catalytic action of the metal. As example was mentioned the decomposition of formic acid into hydrogen and carbon dioxide which takes place when in contact with iridium or rhodium, but not with platinum or palladium. Overvoltage cannot here be the cause, for hydrogen goes off at the platinum without overvoltage. As a good instance of the phenomenon of overvoltage which has not yet been described as such, the speaker instanced the behavior of metals in chromous chloride. Chromous chloride is such a powerful reducing agent that a strongly acid solution evolves hydrogen of itself; when platinized platinum is immersed in a weak solution then hydrogen is also evolved. Measurement of its reduction potential, i. e. of the maximum pressure with which hydrogen is set free cannot be made in this way, as hydrogen is already evolved on platinized platinum at atmosphere pressure. Electrodes on which hydrogen has an overvoltage are charged to a higher potential when introduced into the solution. In the same way the potential of a metal when immersed in a solution which evolves oxygen, e. g. H_2O_2, NaClO, etc., differs according to the overvoltage which oxygen has on the metal.

In the discussion Loeb said that in the name "overvoltage" we use to comprehend a great many phenomena which are essentially different from each other; for instance, the cases in which the electrodes are inert and those in which they have a certain, solution tension are distinctly different. Foerster called attention to the fact that the potential at which oxygen is developed at platinum anodes, continually rises during electrolysis up to a maximum; this rise of potential determines the oxidizing power of the anodic oxygen; on account of this rise of potential electrolytic oxygen often causes complete oxidation; this is the more the case the lower the temperature, because with higher temperatures the rise of the potential is smaller. Coehn has not observed such a rise of potential at nickel anodes; he believes that in Foerster's case some higher oxide of platinum is formed which has a greater overvoltage than pure platinum. Tafel does not believe that this phenomenon can be explained by the formation of a higher oxide, because the same rise of potential observed by Foerster at platinum anodes also sometimes takes place on cathodes. He also pointed out that in speaking of catalytic action of metals it is important to distinguish whether the catalytic action of the metal influences directly the electrochemical oxidation or reduction, or whether it influences subsidiary processes of purely chemical nature; it is very difficult to decide this question experimentally. Bodlaender, Coehn, Woehler, LeBlanc, Buchner, von Euler, and Nernst also participated in the discussion.

The Dissociation Pressure of Soda Solutions.

A paper on this subject, presented by Kuester, is not electrochemical, but shows that the pressure of carbon dioxide from solutions of alkaline carbonates decreases gradually when the solutions become poorer in $NaHCO_3$ and richer in NaOH.

The Preparation of Barium.

A paper on this subject was presented by Guntz. The barium was prepared by careful heating of 3 per cent barium amalgam, which had been obtained by means of $BaCl_2$ solution with mercury. The barium is white; heated with NaCl, compounds of the form NaCl, BaCl, are obtained. These are formed always when melted $BaCl_2$ is electrolyzed.

Replying to a question of Bodlaender; Guntz gave the figures which show that the double iodide has the formula NaI, BaI, 32 per cent Ba, 60 per cent I and 7 per cent Na were found.

Session on June 6.

Application of a Formula of Gravitation to the Process of Diffusion.

A paper on this subject was presented by E. Solvay, of Brussels. As the formula has not been experimentally proved its derivation and details may be omitted. The substance of it is as follows: If we have two miscible liquids, a heavy one and a light one, arranged in layers above each other, the heavier one being below, then the heavier liquid diffuses upwards against the force of gravity. There is a certain relation between the counteracting forces of gravity and of diffusion from which one can calculate the force required to separate a mixture into its two components. What is applicable to the force of gravitation must also apply to centrifugal force, and it

must, therefore, be possible to effect a separation by centrifugal motion.

In the discussion Bredig remarked that this relation had been shown thermodynamically by Gibbs, Gouy, Chaperon and Duhem, and that Gay Lussac had erected long glass tubes containing solutions of NaCl in the Paris Astronomical Observatory, and had investigated whether there was any variation in concentration at the upper and lower ends of the tubes, and that he found no difference. Van't Hoff and Bredig had experimented with a mixture of HI and hydrogen in a centrifugal machine and obtained a slight separation. The effect is, however, very small, and there is no prospect of separating air by centrifugal motion at one operation; by repeating the operation a great many times this very important problem might eventually be solved. Van't Hoff remarked that Solvay's formula might, perhaps, be tested with a mixture of iodoform and benzene, the densities of which are very different.

Note on the Kinetics of Reaction of Reduction Methods.

H. Goldschmidt, of Christiana, presented a paper on this subject. The electrolytic reduction of nitro-compounds to amido-compounds take place in two steps. First nitroso-compounds are formed and these are then further reduced to amido-compounds. Goldschmidt found that the reduction of m-nitrobenzol sulphonic acid by $SnCl_2 + HCl$ is similar to the above. The velocity of the reaction is proportional to the concentration of $ZnCl_2$, instead of being proportional to its third power, as it must be if the reduction to the amido-compound were direct:

$$R.NO_2 + 3SnCl_2 + 6HCl = RNH_2 + 2H_2O + 4SnCl_4.$$

In accordance with the equation

$$RNO_2 + SnCl_2 + 2HCl = RNO + H_2O + 3SnCl_4$$

the reaction must therefore give first a nitroso-compound. It is the velocity of this reaction which is measured. The further reduction by means of $SnCl_4$ to an amido-compound has a velocity too great to be measured, as has been shown in the reduction of nitroso dimethyl analin chlorhydrate, and of p-nitrophenol. Moreover, in accordance with the second equation the velocity of the reaction should either be proportional to the square of the concentration of HCl or independent of it. This is not the case. A possible explanation for this is that the stanno ions do not participate in the reaction, but that an acid $HSnCl_3$ is first formed which then enters the reaction. That the stanno ions, as such, play no part in the reaction, can be seen from the fact that by using $SnBr_2$ and HI instead of the corresponding Cl compounds, one finds a velocity equation of the same form, but a velocity constant about 7½ times as large as with chlorine. The observation that the reduction is so much more rapid with $SnBr_2$ than with $SnCl_2$ might be of value to the preparative organic chemistry.

In the discussion Sackur said that if $SnCl_2$ dissociates at all, it forms univalent cations only

$$SnCl_2 = SnCl' + Cl'$$

similar to the dissociation of $PbCl_2$; he asked whether the observation of Goldschmidt could not be explained in this way. Goldschmidt promised to consider this explanation. Van't Hoff suggested isolating the intermediate product, namely, the nitroso-compound, by shaking. Elbs pointed out that Goldschmidt's observation is a very welcome supplement to Haber's scheme (compare the following paper).

The Importance of Electrochemistry for Preparative Organic Chemistry.

A paper on this subject was presented by K. Elbs. In organic chemistry the application of electrolysis to preparative purposes is far more limited than in inorganic chemistry; nevertheless, the electrochemical processes for the production of carbon compounds has already attained considerable importance. For the preparatory electrochemistry of organic substances three fields come into consideration: The electrolysis of organic acids, the electrochemical reduction, and the electrochemical oxidation. In the present stage of development the electrochemical reduction is far more important than the other two fields for various practical applications.

The electrolysis of organic acids will likely never lead to methods of far-reaching usefulness, and there are at present so many difficulties in the way of electrochemical oxidation that very few successes have been attained. Whether it will be possible to overcome these difficulties to some extent we are at present unable to say.

In the case of electrolysis of organic acids, the aromatic acids do not come into consideration, as their alkaline salts break up at the anode, under evolution of oxygen, and regenerate the acid. In the case of the acids of the fatty series, the discharged anions react with one another in three different ways. Every one of these is sometimes useful as a process of production; from sodium acetate about 90 per cent ethane can be obtained

$$2CH_3.COO = CH_3.CH_3 + 2CO_2;$$

from sodium proprianate 60 per cent ethylen:

$$2CH_3.CH_2.COO = CH_2.CH_2.COOH + CH_2.CH_2 + CO_2;$$

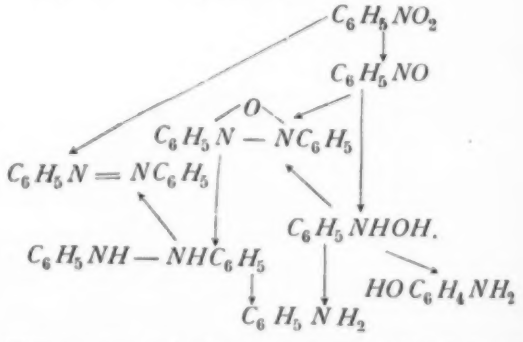
from sodium tri-chlor-acetate 40 per cent tri-chlor-methyl-ester of tri-chlor-acetic acid

$$2CCl_3COO = CCl_3.COO.CCl_3 + CO_2.$$

The preceding carboxyls do not take part in the electrolysis. On this fact is based the important electrosynthysis of symmetrical di-basic acids, for example, the formation of adipic acid in the form of its diethylester from potassium succinate:

$$\begin{array}{l} CH_2.COOC_2H_5 \\ | \\ 2\,CH_2.COO \end{array} = \begin{array}{l} CH_2.COOC_2H_5 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2.COOC_2H_5 \end{array} + 2CO_2$$

The *electrochemical reduction* makes use of the reducing action of the discharged cations, and is considerably successful in the reduction of aromatic mono-nitro and carboxyl compounds. The extensive field of the electrolytic reduction of aromatic mono-nitro compounds is best illustrated by Haber's well-known scheme, to which universal validity may be attributed, the perpendicular arrows denoting processes of reduction, the oblique ones other processes.



With vigorous reduction in moderately acid solution, the corresponding amine is obtained from the nitro-compound. The critical stage of the process is the hydrozyl amine. In a too strongly acid solution it changes over into amidophenol, and with too little acid or too feeble reduction into azoxybenzene. By using lead cathodes, or by adding tin or also copper compounds the nitro-group can be readily converted into the amido-group. This is an excellent method for the formation of amines.

The transformation of hydroxylamin into aminophenylen has only a very limited application as a method of preparation. By moderate reduction in alkaline solution hydroxylamin condenses rapidly and completely to the azoxy compounds; the

latter, being liable to further reduction to the hydrazo form, is generally difficult to obtain. The last-named substance is oxidized by the remaining nitro-compounds, and simultaneously by the oxygen of the air to the azo form. This makes it an easy matter to obtain an excellent output of azo compounds. The same remark applies to the hydrazo compounds, which in general cannot be readily further reduced, and therefore constitute the final product of reduction in alkaline solutions.

The electrochemical reduction of carboxyl groups is successful only on cathodes which have an overvoltage, especially on lead cathodes. Three stages of reduction are to be considered.

1. $2\!>\!C=O+2H=\!>\!C\cdot OH$ | $>\!C\cdot OH,$
2. $>\!C=O+2H=\!>\!CH\cdot OH,$
3. $>\!C=O+4H=\!>\!CH_2+H_2O.$

In the reduction of ketones, reactions 1 and 2 usually take place, 1, the penacone synthesis more readily in acid, 2, the formation of alcohol more readily in alkaline solution:

1. $2CH_3.C_6H_4.CO.C_6H_5 + 2H = CH_3.C_6H_4.C(OH).C_6H_5$ | $CH_3.C_6H_4.C(OH).C_6H_5$
2. $C_6H_5.CO.C_6H_5 + 2H = C_6H_5.CH(OH).C_6H_5$

With acid amides and imides and derivatives of uric acid 3 is generally the principal reaction:

$$\begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CN \end{matrix}\!>\!NH+4H=H_2O+\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CO \end{matrix}\!>\!NH.$$

Electrochemical oxidations by means of discharged anions are in no direction so well under our control, as the reduction by means of discharged cations. To begin with, the selection of a suitable solvent offers considerable difficulties. One can scarcely speak of general electrochemical methods of oxidation, but rather of special processes, such as the oxidation of ethyl alcohol to iodoform, and a few similar cases which allow of no generalization.

THE IMPORTANCE OF ELECTROCHEMISTRY FOR TECHNICAL ORGANIC CHEMISTRY.

M. BUCHNER, of Mannheim, presented a paper on this subject. While electrolysis has come to be of enormous importance in the production of inorganic compounds, many obstacles retard the introduction of electrochemical methods in the technology of organic chemistry. Most organic compounds are non-conductors of electricity, and the anodic and cathodic products of decomposition of the few organic compounds which are electrolytes have no industrial value. Furthermore, the products of electrolysis, instead of being the simple compounds which are desired, are usually complicated mixtures. It is quite natural that electrochemical methods are only adapted as auxiliary, though very important for the manufacture of organic compounds. The first instance of an electrolytic method attaining decisive importance is in the manufacture of indigo, a process now carried out on a large scale.

Owing to the high price of Weldon chlorine, and the great dilution of Deacon chlorine, chemically made chlorine is not suitable for this purpose, so that the Baden Anilin and Soda Fabrik has erected a 3000 to 4000 hp. plant for the electrolytic decomposition of sodium chloride. The Griesheim-Elektron process is used. It has the great additional advantage that simultaneously the alkali required in the indigo smelting is produced at the cathode.

A process of similar importance is the electrolytic oxidation of chromium sulphate to chromic acid by the well-known process of the Hoechster Farbwerke for the manufacture of alizarin. The process is a so-called electrolytic regeneration process. Its essential technical advantage is that the same amount of oxidizing agent always remains in use and consequently the capacity for oxidation is almost unlimited. By means of an ingeniously constructed cycle the same sulphuric acid passes without loss continually through the steps of manufacture, furnishing the necessary oxygen.

Finally, may be mentioned the importance which inorganic electrolytic processes have for the so-called finer preparative organic chemistry, as, for example, the electrolytic production of metallic sodium, great quantities of sodium being now consumed in the manufacture of potassium cyanide; if sodium amide is adopted for the manufacture of indigo, the demand for electrolytic sodium will be greatly increased. The reduction of nitric acid in acid solution to hydroxyl amine is technically very important in the production of organic compounds.

While the direct electrolytic reactions are at present of no practical utility, the second class of electrolytic reactions—those which accompany the electrolysis of inorganic electrolytes, acids, salts and bases, by which the organic substances present in the electrolyte are oxidized, chloridized, iodized or reduced—are of great importance for technical chemistry. The ordinary chemical oxidation or reduction of an organic substance with an oxidizing or reducing agent, which is prepared in a separate process, consists of two steps: the manufacture of the oxidizing or reducing agent, and the oxidation or reduction itself. It is here of no account whether the same factory carries out both processes or not. In either case the expenses for material, apparatus, sinking fund and labor have to be paid. By carrying out the oxidation or reduction electrolytically, the two separate processes are merged in one common simplified process, thus reducing the costs of apparatus, material, labor and sinking fund. The one operation can, of course, not be carried out without an equivalent expenditure of energy for the production of the oxidizing or reducing agents. Notwithstanding the necessity of an extra mechanical plant, the combined process means a technical simplification. The electrolytic oxidation or reduction of organic compounds does away with intermediate operations, allows a simplified development and manufacture of much purer products, and finally surpasses the purely chemical process because by dividing the cell into compartments by means of diaphragms, several chemical substances may be produced simultaneously, and a certain amount of electrical energy required for the electrolysis can be saved.

The technical application of the anodic processes to the electrolytic production of organic compounds has made up to the present time very little progress. There are as yet no methods of general importance. On the other hand, through the brilliant work of Elbs, Gatterman, Haber, Haeusermann and Loeb, the field of electrolytic reduction, especially of aromatic nitro-compounds, has been opened to the application on an extended scale. The principal products of the reduction of aromatic nitro-compounds which are of technical importance are the amido phenols, hydrazo compounds, and amines. The former can be made, according to the patented process of Friedrich Bayer & Co., in Elberfeld, by the electrolytic reduction of nitro hydro-carbons of the benzene series in sulphuric acid solution.

When one considers that the use of zinc for the production of hydrogen is expensive, and that in this method the alkali which is required for the reduction is lost, the outlook for the electrolytic manufacture of hydrazo compounds appears very promising. For this reason it has been the object of numerous patents. Especially to be mentioned are those of the anilin factory of A. Wuelfling in Elberfeld, covering the well-known Elbs methods of reduction, and of the dye works of Friedrich Bayer & Co. in Elberfeld. The technical value of the latter process lies in an enlargement of a method of Elbs' for the electrolysis of nitro-benzene suspended in alkaline alcohol,

with lead and mercury cathode. In the modification of this method cathodes of metals whose oxides are soluble in alkali, are used in an aqueous solution of alkaline metal salts, so that the cost of current is distributed between several products.

The lack of a practical method for the electrolytic manufacture of aromatic amines, which are used in great quantities in the manufacture of dyes, lead the author to develop the following processes patented by C. F. Boehringer & Soehne in Mannheim-Waldhof (German patents 116,942, 117,008, 121,835, 123,813, 127,815, 130,742 and 132,404). Tin is chemically capable of producing the reduction; in order to produce the reduction with small quantities of tin, Buchner introduced a small quantity of tin into the space at the cathode. The cathode is made of a chemically inactive material and is surrounded by the nitro-compound which is to be reduced. The tin dissolves in the presence of the nitro-compound, reducing it to the corresponding amine, and is deposited again on the cathode. Further developments of the process showed that iron, lead or copper may be substituted for tin, other conditions remaining unchanged. While in this scheme for the electrolytic reduction of nitro-compounds in alkaline alcohol solution, Haber had already foreseen the theoretical possibility of reducing nitro-benzene to anilin, yet practically this reduction could not be realized, because by the reduction in alkaline solution only a azoxy-azo and hydrazo-benzene were obtained. He has now found that a copper cathode, or any other cathode, with addition of powdered copper, has the excellent property of electrolytically reducing aromatic nitro-compounds, of whatever constitution, suspended in alkali to their corresponding amines. The process depends on the fact that the velocity of reduction by hydrogen in the presence of copper is so great that the processes of condensation, which, with other electrode material, lead to azoxy-azo and hydrazo compounds, fall entirely in the background.

It is thus possible to combine the electrolytic production of amines with an entirely different electrolytic process of the electrolytic decomposition of alkali chlorides, a process already operated on a large scale. The hydrogen evolved by the electrolysis of alkaline chlorides is generally a dead loss, there being no application for it. Moreover, the generation of hydrogen, on account of the cathodic polarization, requires the expenditure of a certain e. m. f. By adding to the electrolyte in the vicinity of the cathode a depolarizer in form of an aromatic nitro-compound, a two-fold advantage is gained; the hydrogen which would otherwise be wasted is used economically in reducing the nitro-compound, and the pressure which is required for the electrolysis is reduced, thus giving a much greater yield with the same expenditure of energy.

The following example will serve to illustrate how this method may turn hitherto useless waste to good commercial advantage: The German inorganic chemical industry produces yearly 50,000 tons of bleaching powder by the electrolysis of alkali chlorides; this corresponds to 500 tons electrolytic hydrogen which escape unused. The electrolytic combustion of this amount of hydrogen with the oxygen of aromatic nitro-compounds at a suitable cathode, would produce 17 billions of kilogramcalories; moreover, the saving due to depolarization would at the same time produce 9,000,000 kg. of anilin—about three-quarters of the annual consumption of the entire world, and incidentally make a saving of 11,000,000 kg. of iron at present required in the manufacture of anilin.

PRODUCTION OF POTASH IN GERMANY AND THE KALI SYNDICATE.

A recent consular report contains the following translation of an article, recently published in the *Deutsche Industrie Zeitung*:

"The German potash-producing industry has attained considerable importance within a comparatively short time. Its fame has gone beyond national boundaries. Over $49,980,000 are invested in Germany in this industry, not counting the capital of the numerous boring or drilling companies which the Prussian financial department has invested in its potassium mines. The number of workmen employed in this industry in the Empire is about 30,000 and the value of the product nearly $13,804,000. The importance to which the industry has attained is due to the efforts of the German Kali Syndicate. The prices secured by this organization must be regarded by their most bitter opponents as of the greatest value to the national industries.

The German agricultural classes ought to look upon the acts of the Kali Syndicate as particularly advantageous to them, not only in the fight for better prices which resulted in the potash fertilizers being sold much cheaper at home than they are abroad, but especially because of the potash propaganda of the syndicate which resulted in extending the uses of potash as a fertilizer. The consumption of kainite, inclusive of Hartsalz and sylvanite, increased from 175,000 tons in 1890 to 825,000 tons in 1902. On each 247 acres of arable land 862 pounds of potash were used in 1902, while only 156.5 pounds were used in 1890. This enormous increase would have been unthinkable but for the well-planned and energetic efforts and activities of the syndicate. A single company would have found such efforts and results absolutely impossible. The regulation of prices by the Kali Syndicate is very much better from another standpoint. The fact that foreign countries have to pay higher prices makes it possible for the syndicate to sell its products to German agriculturists a great deal cheaper than would be possible could the syndicate not regulate price and production. This campaign of price, in which the great German agricultural population has considerable interest, can be successfully continued only so long as the foreign consumers of potash do not succeed in obtaining a foothold in the Empire's commercial markets and mines. The recent efforts made by Americans—supported, we regret to say, by some Germans—to exercise a controlling influence over the German potash works must be regarded from a national standpoint as objectionable. Should these efforts nearly or even partially succeed, the potash market must receive a great shock and the continuance of the syndicate be made questionable. With the syndicate stands or falls the question of profit in the mines and mills of the German potash companies. For the number of the works their enormous capacity to produce is such that an entrance or an introduction of foreign competition would result in throwing the potash market into convulsions; at the same time, the possibility of finding profitable markets after the suppression of the syndicate would be very small.

The industrial crash of a great number of potash factories would be the inevitable result of any such change. If those in the syndicate and those outside wish to avoid the loss of markets and reduction in prices, they must look to a renewal of the contract with the syndicate.

These works, which will one day want to enter the syndicate, and which are endangering the position of the syndicate at the present moment by their unreasonable demands—particularly dangerous because of the present movement among the Americans—should keep their eyes open at this critical moment. They can endanger not only the success of the syndicate, but its very existence. If the syndicate can be continued, the hope of further development of the potash industry can be depended upon; but no one must be deceived into believing that the large profits of the past can ever again be realized."

BOOK REVIEWS.

Secondary Batteries, Their Theories, Construction and Use. By E. T. Wade, London: The Electrician Printing & Publishing Co. Price $4.00.

This book is certainly valuable on account of the description

of many types of storage battery cells, both of historical interest and of actual importance. For the reader not well acquainted with the matter, it would be more valuable, however, if instead of giving a mere description of the numerous types of construction a criticism of each were made pointing out its advantages and its faults. In the historical review of the alkaline cells all the older cells of the copper-zinc type are described, but it is remarkable that the more modern development of these cells is not discussed, with the one exception of the Edison cell. For example, Jungner is entirely ignored.

What is said about manufacturing processes and the use of secondary batteries is valuable too, though naturally such a book cannot contain information on up-to-date manufacturing methods kept secret by the manufacturers.

The theoretical part of the book, however, needs improvements. The author takes the standpoint of the classic investigations of Gladstone, Hibbert and Tribe, but he does not accept the doctrines of modern physical chemistry in their application to the lead cell. The ionic theory of the lead cell may indeed be interpreted in rather different ways, and may, therefore, be regarded as somewhat uncertain, but some of the applications of modern physical chemistry to the lead cell are quite independent of any particular hypothesis, and should be referred to in a book dealing explicitly with the theory. The theories of modern physical chemistry have proven here so useful that, as Dolezalek points out in the introduction to his well-known book, there is, perhaps, no other case in which these theories are applicable with such a degree of exactness, and in which their value manifests itself so much as in the explanation of the phenomena of the lead accumulator.

A consideration of the principles of thermodynamics would have been particularly valuable, as it would have shown at once the impossibility of the author's theory of the formation during discharge of a long series of lead compounds with gradually varying SO_4 content.

That the drop of voltage during discharge is due to internal resistance is an idea still frequently entertained by some other authorities besides Wade; but a series of careful measurements carried out and afterwards published by Dolezalek and Gahl have clearly proved that this is not so. Although the resistance certainly increases upon discharge it does not do so nearly enough to account for the sudden drop of voltage at the end; and the true explanation of the phenomenon is to be found in the fact that the acid contained in the pores of the plate becomes more and more diluted. The electromotive force, therefore, becomes lower and lower, just as if the acid of the whole cell were decreasing in the same degree. The drop of voltage is increasing in speed, as for very dilute acid the voltage is influenced by concentration changes much more than for solutions of higher gravity.

It may be hoped that a new edition will bring this book to a modern standpoint and make it a thoroughly reliable book on the subject of storage batteries.

CURRENT NOTES.

ELECTROLYTIC PRODUCTION OF BLEACHING LIQUORS.—The article by Dr. W. H. Walker, published in our September issue, contained two typographical errors. On page 441, left-hand column, middle of the page, the parenthesis should read: "When working a nine or ten per cent brine." The other correction is in the same column, last paragraph. The firm name "Siemens-Halske Co. of Berlin" should read "Siemens-Schuckert Co., of Berlin." This company manufactures the apparatus shown in figure 8, on page 442.

NEW MEMBERS OF THE AMERICAN ELECTROCHEMICAL SOCIETY.—At the meeting of the Board of Directors, held at Niagara Falls on September 17, the following gentlemen were elected members of the society: William H. Davis, Bear, Idaho; Dr. Michael Lark, Lockport, N. Y.; James F. McElroy, Albany, N. Y.; William Valentine, Lansingburgh, N. Y.; Prof. Elihu Thomson, Swampscott, Mass.; Henry H. Seabrock, Washington, D. C.; E. E. Armstrong, Niagara Falls, N. Y.

THE IRON AND STEEL METALLURGIST.—Announcement is made that *The Metallographist* is to be published under the title, *The Iron and Steel Metallographist*, beginning with January 1, 1904. The enlarged magazine is to be devoted to the development of the iron and steel industry. Messrs. Sauveur and Whiting are the editors.

THE WESTERN CHEMICAL MANUFACTURING CO., of Denver, Col., have issued a very neat little Chemists' Handbook, of convenient size to carry in the pocket. It contains much useful information, concerning impurities in c. p. acids and tests for same, rapid assay methods for metallurgists, assaying of blast furnace slags, standard solutions, weights and measures, specific gravities, etc. A table of atomic weights is added with brief information concerning the properties of the elements and rules for qualitative tests. The information given in the book appears to have been carefully collected, and the handy little book should be quite useful to chemists and metallurgists.

CORRESPONDENCE.

CYANIDE SILVER PLATING BATHS

To the Editor of ELECTROCHEMICAL INDUSTRY.

Sir—I have read with great interest an abstract of an article published on page 465 of the September number of your journal on the decomposition of cyanide silver plating baths. The statement therein that the cause of the loss of cyanide which makes the regeneration of such baths necessary after a time, had not been ascertained, is hardly borne out by the facts; the cause referred to is now known by many engaged in the electroplating art as a very simple equation, as will appear later on.

Is not the expression, " loss of cyanide," somewhat misleading? Technically, the term "cyanide" implies a combination, as cyanide of potassium, cyanide of silver, etc. The metallic bases unite with the cyanogen CN of hydrocyanic acid HCN to form the cyanides.

Now, it is well known in the anhydrous state, both cyanogen CN and its component HCN are not readily decomposed by either air or light, but their aqueous solutions gradually break up into a series of different substances, as oxalic, formic, ureamic acid and ammonia, and other combinations; in a plating bath, a portion of cyanogen CN, as hydrocyanic gas, also passes off in the free state from the moment such solutions are formed; heat and excessive light also greatly accelerate this evaporation and decomposition.

It is also true, as stated by Messrs. Jordis and Stramer, that the loss of cyanogen CN is much greater in a solution while under electrolysis than when idle. As known, when a solution of potassium cyanide is freshly made and bottled up, so as to be airtight, it will be found, when opened after a long time, to be as efficient as when freshly made, if not exposed to too strong a light.

My experience with potassium cyanide plating solutions many years ago does not agree, however, with the result obtained by authors referred to in the statement that the use of silver chloride in the bath results in less resistance to the current as compared with the pure cyanide bath. Just the reverse was the case, and for this reason, the formation and deposition of insoluble potash salts on the anodes during electrolysis, as the cyanogen disappears, not only greatly increases the resistance, but the solution is robbed of its metal just in proportion as the component of cyanogen is diminished, and renders the anodes incapable of replenishing the metal deposited on the cathode, because their coating of oxide and potash salts becomes more and more insoluble as the solution loses its cyanogen.

Hence, in preparing such a bath I always preferred to make up the solution with either the cyanide of the metal, or dissolve

the proper amount of metal in a solution of potassium cyanide by the battery process, so as to eliminate as far as possible the accumulation of an excess of potash or other salts in the solution. For this reason it is more economical to use the pure potassium cyanide rather than the cheaper commercial article. But with the best of such solutions, deterioration and decomposition soon set in, and it is necessary to replenish the wasted energy of the bath. Unfortunately, as the cyanogen CN decomposes and passes off it leaves the potash salts behind to clog and slime the anodes—for the solvent power of such solutions to remove the anodic oxidation products rests entirely with the CN, or HCN, and is in proportion to their amount present in the bath.

To minimize the accumulation of these salts, I had recourse to a plan which I found to be very satisfactory. Instead of adding fresh potassium cyanide from time to time, as is customary, I passed HCN gas into the solution by decomposing under the well-known formula yellow prussiate of potash with dilute sulphuric acid in a lead retort over a gas flame, passing the gas HCN through a wash bottle, thence by tube directly into the plating solution. The uncombined potassium carbonate readily dissolved the gas, and the bath was at once restored to its original condition, and any insoluble coating on the anodes, left from the last electrolysis, would be instantly dissolved. Thus, the active oxidation of the anode and solution of the metal was completely restored. This introduction of HCN was repeated as often as the cyanogen diminished.

It is customary with some platers to use an aqueous solution of commercial HCN in their plating baths instead of potassium cyanide as a regenerator, but it is a dangerous and expensive article to keep on hand, exceedingly poisonous, and soon decomposes unless carefully sealed up and kept from the light.

Regarding the use of silver chloride in plating baths, while I do not recommend it as compared with silver cyanide, yet excellent plating solutions are so made and used. I have repeatedly used it, but for reasons stated prefer either the silver cyanide or the battery process described. The statement of Jordis and Stramer that in a bath of silver chloride the loss of cyanide and increase of "carbonate" is greater than with the use of pure potassium cyanide, seems to me to involve an erroneous equation; also their further statement that the increased formation of "carbonate" must have been brought about by an increased anodic oxidation caused by chlorine ions is unintelligible. As there is put into the solution so many units of potassium cyanide, I fail to see how the loss of "cyanide" can result in increasing the "carbonate."

The function of potassium carbonate in the preparation of potassium cyanide is to absorb and dissolve the HCN. Now, when the latter disappears, it simply leaves behind an equivalent of uncombined potassium carbonate, but it simply could not increase the latter—nor do I comprehend how, when silver chloride is used, increased anodic oxidation could be caused by chlorine ions.

It would be more in accordance with the chemical action observed to state that the disappearance of cyanide, where silver chloride is used, would cause an equivalent of chlorate to combine with an equivalent of potassium carbonate to form a complex subsalt. The fact is that the disappearance, passing off or decomposition, call it what you may, of the CN from a plating solution, simply leaves an uncombined portion of the potassium carbonate or other salts in the bath, and a restoration of the CN or HCN is all that is required to restore the same to full working efficiency. The process I used, as described, gave the best results, as it ensured the non-loading of the bath with troublesome salts. To sum up, therefore, I can state that the cause of the loss of "cyanide" (cyanogen) in plating baths is well known in the art, namely, that it is owing to the unstable character of HCN, which, when passing off, leaves the solution inert.

Again, can a bath containing silver chloride be used? It certainly can, and is used every day with good results, but is not equal to the silver cyanide bath. The statement of Jordis and Stramer that more cyanide disappears than is equivalent to the amount of "carbonate" found, is contradicted by their first statement, that the loss of cyanide is accompanied by an increase of "carbonate." Perhaps the translation is at fault. Their statement, however, that freshly made baths are entirely satisfactory is quite correct. A plating bath begins to degenerate from the hour it is made, because of the unstableness of the chief solvent, the HCN.

Cincinnati, Ohio. James Powell.

To the Editor of Electrochemical Industry.

Sir—The translation of the article referred to by Mr. Powell is correct. The authors do not, however, make the statement in the original, nor is it made in the translation, that the loss of cyanide is "accompanied" by an increase in carbonate; they simply say that "the loss of cyanide and the increase in carbonate is always greater with the working bath than with the idle one, etc.;" nothing is said about the ratio of such loss and increase. The contradiction referred to by Mr. Powell, therefore, does not exist. "Loss of cyanogen" necessarily involves a loss of cyanide.

Compiler of the Synopsis.

AN ALLEGED SUBOXIDE OF SILICON.

To the Editor of Electrochemical Industry.

Sir—In the discussion following my paper at the recent meeting of the American Electrochemical Society, Mr. Cowles asked if I had ever found any evidence of the existence of a suboxide of silicon in carborundum furnaces. He stated that Prof. Mabery had analysed a certain amorphous substance, apparently resembling the so-called "white stuff," produced in the Cowles furnace in 1885, and had found that it was a "suboxide of silicon."

I do not know what methods Prof. Mabery employed in his examination of this substance, but a possible explanation of the results he obtained has occurred to me.

Colson and Schutzenberger described certain experiments with silicon, in which they produced a compound having the formula Si_4C_4S, which on oxidation yielded a body having the formula $Si_4C_4O_2$ (*Comptes Rendus* 92, p. 1508 and 94, p. 1526).

Acheson has described certain compounds containing silicon, carbon and oxygen in various proportions corresponding to formulæ, such as Si_2C_2O and Si_7C_7O. These compounds seem to vary in their composition as regards the amount of oxygen present, although the carbon and silicon are in a definite ratio—one atom of carbon to one atom of silicon. One of the possible compounds would be Si_4C_4O. In the following table are given the theoretical compositions of SiO and Si_4C_4O, and, omitting a small amount of iron and aluminium present as impurities, the composition of a substance produced by Mr. Acheson in one of his furnaces:

	SiO	Si_4C_4O	Substance from Acheson furnace.
Silicon	63.96	63.96	63.4
Carbon	....	27.03	26.8
Oxygen	36.04	9.01	9.8
	100.00	100.00	100.0

Comparing these figures it seems possible that it was some substance approaching the composition of Si_4C_4O that was produced in the Cowles furnace, and that Prof. Mabery, failing to discover the carbon present in the specimen, concluded that it was a suboxide of silicon.

It must be remembered that at the time of Mr. Cowles' experiment the compound silicon carbide (SiC) was unknown, for the crystalline form was first described by Acheson in his United States Patent, February 28, 1893 (applied for May

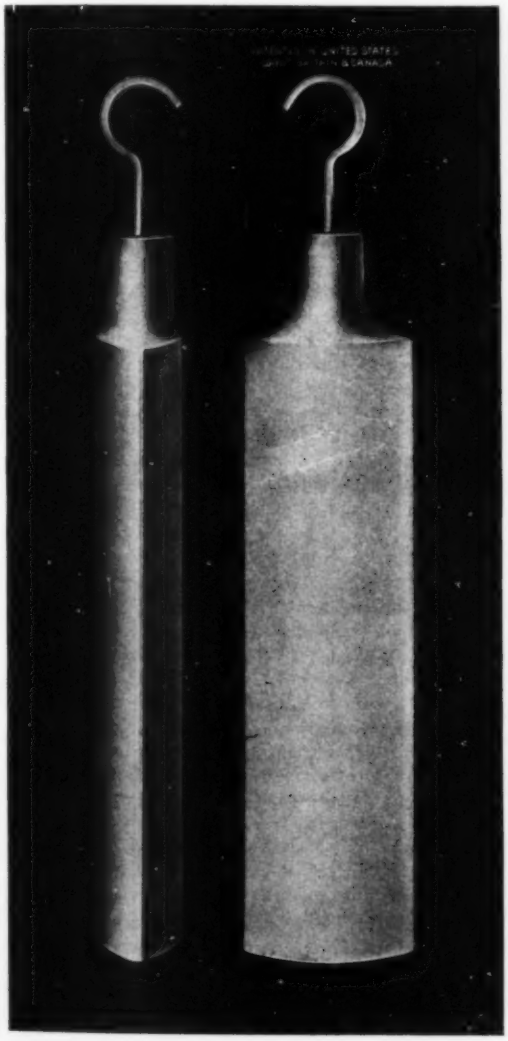
10, 1892), and the amorphous form by Schutzenberger in 1892 *Comptes Rendus*, t. CXIV., p. 1089. While it is true that the work of Colson and Schutzenberger, referred to above, dealing with the compounds of carbon, silicon and oxygen, was published as early as 1881-1882, this work does not appear to have been very well known.

FRANCIS A. J. FITZGERALD

NIAGARA FALLS, N. Y., September 21, 1903.

ELLIPTIC ANODES FOR NICKEL, COPPER, ZINC, ETC., PLATING.

The adjoining illustration shows a form of anode for electroplaters which has just been placed upon the market by the Hanson & Van Winkle Co., of Newark, N. J. This company, which is one of the pioneers in the electroplating industry in this country, has realized the importance which the use of a suitable form and material of the anode has for a good deposit on the article to be plated. This fact has not been



ELLIPTIC ANODES FOR ELECTROPLATING.

thoroughly appreciated by electroplaters in the past, but recent investigations have shown that the proper form of the anode is of great practical importance.

In the June issue of this journal appeared an article by Prof. C. F. Burgess and Mr. Carl Hambuechen, of the University of Wisconsin, in which they gave an account of a thorough test of anodes with elliptic cross-section compared with the ordinary flat anodes of rectangular cross-section. The authors pointed out that the important point is to get a large active anode surface, which does not mean merely the area of surface exposed to the electrolyte, but rather the area from which current passes readily into the electrolyte. They found that with an anodic cross-section the current density over the surface is much more uniform, so that the anode is uniformly corroded all around until it is reduced to a very thin rod or strip. The waste is thereby very considerably reduced.

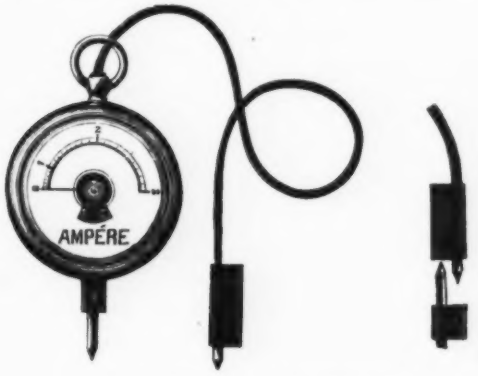
The Hanson & Van Winkle Co., who manufacture such anodes of elliptic cross-section in nickel, zinc, copper, etc., under patents in the United States, Great Britain and Canada, state that these results of the above scientific investigation are being fully confirmed by electroplaters in commercial practice. They have reprinted the article mentioned above with illustrations in their "Green Series" No. 2, which they will mail to anybody interested in the subject.

POCKET VOLT AND AMMETER.

In view of the fact that small and comparatively inexpensive testing instruments are being imported into this country from France and Germany in large quantities for such purposes for which high-priced instruments are not required, the Talmont Electric Engineering Company, 150 Nassau Street, New York City, have designed a small pocket volt and ammeter with a very handy connector.

The instrument which is now being placed on the market is shown in the adjoining diagram. The one pin-connector is fixed to the instrument by a flexible cord, while the second one is loose, and may be easily and quickly screwed into the instrument when it is to be used, or may be pushed into the first one when one wants to carry the instrument in the pocket so that the points of both pins are well protected. The instrument permits easy and quick measurements in connection with a large number of accumulators or primary batteries.

The design of the instrument is based on a patented galvanometer system which is claimed to prevent the readings from being affected by magnetic fields or large masses of iron or by strong currents passing in the neighborhood. All



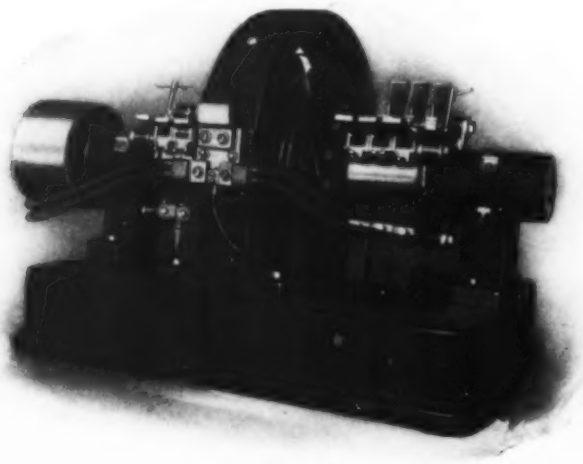
POCKET MEASURING INSTRUMENT.

the conducting metal parts are carefully protected and insulated, which is a point of some importance, as lighting circuits and storage batteries have often earthed contact. The case is nickel-plated and the scale is drawn on white paper.

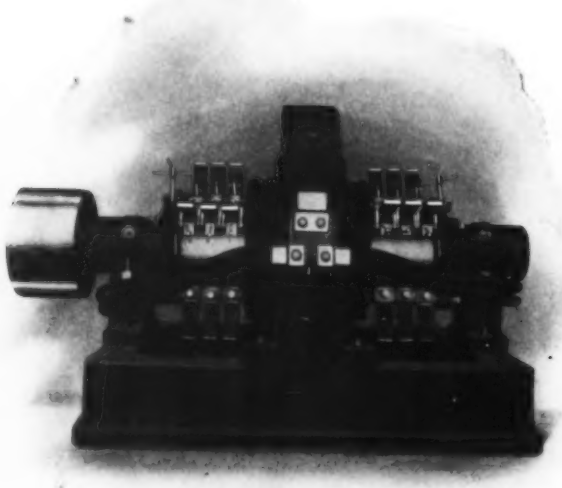
The instrument is said to be just as good as the best German and French instruments of this type; it is a perfectly new model and inexpensive and intended for such purposes in the shop or laboratory for which highly accurate testing instruments are too expensive or too inconvenient.

DYNAMOS FOR ELECTROPLATING, ELECTROTYPING AND GENERAL ELECTROLYTIC WORK.

The adjoining illustrations show a new line of dynamos, specially designed for low voltage and powerful current work, and built by Mr. Charles J. Bogue, 207 Centre Street, New York City. While we have already briefly referred to these machines in our August number, we are now able to describe them more in detail. In these machines all parts liable to need replacing are made strictly interchangeable, so that repairs may be made with a minimum of time and expense.



ELECTROPLATING DYNAMO.



ELECTROPLATING DYNAMO.

By carefully selecting materials and embodying new features in the construction, the designer has succeeded in making the weight per unit of output very low. In the bipolar type the magnetic circuit is composed of a yoke of best grade soft steel accurately fitted and securely bolted to a soft gray iron base, which forms a secondary magnetic circuit in shunt with the yoke, thus reducing the reluctance and utilizing materials, ordinarily wasted. The poles and pole-shoes are in one piece and are made of the same superior grade of steel as the yokes.

The armature is built of carefully insulated punchings of soft decarbonized steel, thoroughly annealed. In the bipolar sizes the punchings are mounted directly on the shaft and keyed securely to the same. The multipolar sizes have the punchings held by spiders and secured by bolts. All sizes have the modern slotted or toothed armatures.

The shaft is of high carbon, crucible machinery steel and is accurately turned. The bearings are of hard phosphor bronze in one piece, and are of ample size to secure cool running, and are continuously and automatically flooded with oil while running. The oil wells are large and open at the top for inspection; they carry enough oil to last one to four weeks with one filling.

The commutators and brushes are of very large size, and are stated to be greater per unit of output than on any machine on the market. The brushes are of fine mesh wire gauze or of soft, thin sheet copper. The commutators are of tempered Lake Superior copper, well insulated with mica. The sleeve is secured to the shaft with a key.

The brush holders are simple; have a good clamp and adjustment and do not stick or bind on the brush stud. The current is carried from the brush to the stud by a heavy flexible conductor, so that the contact between the holder proper and the stud is not depended upon to carry the current.

The speeds of all machines of this line are moderate, and, as the armatures are light and well balanced, the bearings are prevented from getting hot.

For ordinary nickel, cyanide copper or brass plating, as well as electrotyping with two tanks in series, and for cases in which no very exact regulation of voltage is required or where no specially low voltage is needed, the plain shunt-wound type is used. These standard shunt machines are speeded in the smaller sizes (P_1 to P_4) to give 5 volts at no load, and the large sizes to give 6 volts. When running under full load the voltage drops in the smallest machines about 20 per cent, and in the largest sizes about 12½ per cent.

There are, however, two common cases in which the shunt machine is not the best type. One is where nearly absolute voltage is required, as, for instance, for nickel-plating on zinc for certain classes of work. The other case is when an extra low voltage is required, say from 1 to 3 volts, as in silver-plating or when very thick deposits of copper are made in a sulphate solution. In both of these special cases, except with rather small machines, a separately excited dynamo is preferable to the shunt machine. The exciting current for the field magnets is here furnished from an outside source, such as the shop-lighting current or a small exciting dynamo. As the field is maintained in this case entirely independent of the armature current, very fine regulation is possible by means of a suitable field rheostat, even at the lowest voltages in commercial use.

In the following table of standard machines the weights of metal deposited are approximate, but necessarily not exact, as they are subject to variation under different conditions.

	Speed.	Amperes.	Lbs. Nickel in 10 Hours.	Lbs. Copper in 10 Hours.	Oz. Troy Silver in 10 Hours.	Dwt. Troy Gold in 10 Hours.
P1.....	1,600	100	2.4	2.6	130	1,500
P2.....	1,500	160	3.8	4.2	206	2,400
P3.....	1,400	256	6.1	6.6	330	3,800
P4.....	1,300	410	9.8	10.7	530	6,100
P5.....	1,100	656	25.5	17.	850	
P6.....	970	1,000	24.	26.	1,300	
P7.....	780	1,600	38.	42.		
P8.....	700	2,400	57.	62.		
P9.....	550	3,600	86.	94.		

THE EDISON NICKEL-IRON STORAGE BATTERY

The Edison nickel-iron alkaline storage battery which has recently been placed upon the market, has been tested by a number of authorities in the storage battery field. From a report made by Mr. W. Hibbert on tests in England the following details are gathered. The Standard Edison automobile cell is of rectangular shape, 13 inches high, has a cross-section of 5.1 x 3.5 inches, and weighs 17.8 pounds. It contains 14 positive and 14 negative plates. Each plate is made of sheet steel, nickel-plated, punched with 18 rectangular holes. In each of these holes is inserted a flat pouch or pocket containing the active material. The walls of these pockets are perforated by exceedingly fine, short slots to allow easy diffusion of the electrolyte.

Both positive and negative plates are alike, except in respect of the active material. The pockets in the negative plate contain finely divided iron; those in the positive contain "peroxide of nickel." The liquid is a 20 per cent solution of potash. A small quantity of electrolyte suffices as it acts merely as an electrolytic channel for "lifting" the oxygen from one electrode to the other.

The proximity of the plates does not apparently involve danger of short-circuiting. The plates are thin, but being made of steel their rigidity is exceptionally good. Mechanical stability is further assured by vulcanized rubber separators, the whole forming a compact mass, calculated to resist all the ordinary mechanical shocks it is likely to undergo.

The only special mechanical difficulty which seemed probable was the chance that the gases evolved during charging might eject some of the active material from the pockets. During the test, therefore, the pockets were watched carefully, especially during very heavy charges, but without any evidence of loss.

The cell is sealed in its steel case. Two stout connecting pins (from the two sets of electrodes) come through liquid-tight bushings of vulcanized rubber. These pins are made slightly conical, as are also the connectors which fit on them, and the mechanical finish and easy grip of the terminals add to the ease of using the battery. On the top of the case there are also a spring stopper with rubber flange, covering the hole by which the electrolyte is introduced, or distilled water added from time to time (to make up for the loss of water during charging); and a vent hole guarded by a gravity valve. This latter provides for the escape of the gas evolved during charge. The hole and valve are covered by a gauze nipple, which prevents escape of spray while allowing gas to pass. Acting on the principle of Sir Humphrey Davy's safety lamp, the same gauze further prevents any chance of explosion should a flame be brought near to the exit.

The e. m. f. is 1.33 volts. The internal resistance is 0.0013 ohm. The output at a discharge rate of 60 amp. is 210 watt-hours, or 11.8 watt-hours per pound of total weight of cell. The cell recovers its normal voltage almost instantaneously when the current returns to an ordinary value.

In the accompanying curves, Fig. 1 shows the variation of the voltage during discharge at various discharge rates. Each curve corresponds to a discharge at constant current, the discharge rates varying from 30 to 200 amperes. This last is a high rate for a cell of this size, but the test showed that the cell could stand it without injury. It took the succeeding charge in an excellent way, and yielded the 30-ampere curve immediately afterwards. At 120 amperes the output was 91 per cent of the maximum output. Even at 200 amperes, the ampere-hour output is 82 per cent of the maximum.

In Fig. 2 are given the results of one out of many experiments, made to test the flexibility of the cell. The standard cell was discharged, starting at 60 amperes. After 5 minutes the current was suddenly increased to 230 amperes; 25 minutes after start the current was reduced again to 60, and so on, as shown by the curve. The cell having yielded this great current for short intervals, recovered almost instantaneously. It does not appear to be injured in any way, and subsequent charging and discharging seemed to be quite normal. An important point in traction cells is the rate at which they can be charged. Experiments on this point demonstrated that the

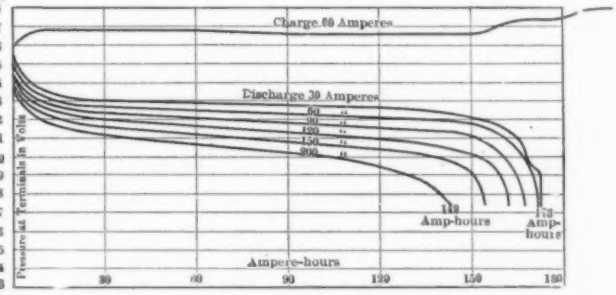


FIG. 1.—DISCHARGE OF IRON-NICKEL STORAGE BATTERY.

Edison cell of the type under test may absorb 70 to 75 per cent of its full charge in one hour. A discharge after a one hour's charge showed that the cell could deliver 124 ampere hours out of the 175 put into it at this high rate.

After three months' work with very many charges and discharges the capacity of the cells was the same as at the begin-

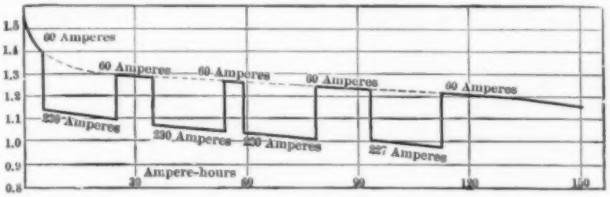


FIG. 2.—TEST OF FLEXIBILITY OF IRON-NICKEL STORAGE BATTERY.

ning. It had neither increased nor diminished. Examination of the plates after three months' work did not indicate any signs of corrosion.

A $25,000 PRIZE FOR THE TREATMENT OF GRAPES

The American Grape Acid Association is offering $25,000 for a process for making grape acid from grapes. They have issued a booklet setting forth their offer in detail, also a placard, of which the following is a copy: "The United States is a very large importer of grape acid, while California is a very large producer of grapes. The surplus of grapes means a quantity of raisins and wine demoralizing to the American market. The American Grape Acid Association has deposited securities with Daniel Meyer, Esq., banker, San Francisco, for the payment of $25,000 to any person who devises a process or formula for the utilization of California grapes containing over 20 per cent of saccharine, worth $10.00 per ton, to produce tartaric acid (perhaps by transforming the sugar in the grape into acid) at a price which would permit exportation without loss. The decision in awarding the amount to rest with three out of five of a jury who have been appointed to determine the matter, whose verdict would be final; the offer to close December 1, 1904. The following gentlemen constitute the jury: Percy T. Morgan, president of the California Wine Association, the largest distributors of wine in the United States; Andrea Sbarboro, president of the Manufacturers' and Producers' Association, of California; C. De Guigne, president of the American Cream Tartar Company; A. Schilling, of the firm of A. Schilling & Co. In case the formula is deemed by the inventor to deserve a larger payment than $25,000, and such process is patented or patentable in the various civilized countries, we ask for the privilege of making an offer for the sole right to use the formula. Co-operation is solicited. We shall

be pleased to mail these offers wherever directed, and publicity given to the enterprise will be appreciated. Address all communications to American Grape Acid Association, 318 Front Street, San Francisco."

PERSONAL.

Messrs. F. A. J. Fitzgerald and P. McN. Bennie, who were formerly connected with the International Acheson Graphite Co., are now consulting engineers for special electrometallurgical work, with headquarters at Niagara Falls.

Mr. Woolsey McA. Johnson has been appointed metallurgist of one of the plants of the Lanyon Zinc Co. He is now located at Iola, Kan.

Mr. Truman H. Aldrich, of Birmingham, Ala., visited Salt Lake recently in order to study the methods of gold extraction.

DIGEST OF U. S. PATENTS

Prior to July, 1902.

Compiled by Byrnes & Townsend,
Patent Lawyers,
National Union Building, Washington, D. C.

White Lead by Electrolytic Methods.—*Continued.*

589,801. September 7, 1897. Herman C. Woltereck, New York, N. Y.

Electrolyte consists of a mixture of an alkali metal bicarbonate and a salt of which the anion forms soluble lead compounds. The two salts are employed approximately in the proportions required by the reaction (one part bicarbonate to four parts of solvent). Lead, carbon dioxide and water are supplied as consumed. Prefers to employ salts of ammonium on account of low voltage required for their decomposition.

625,918. May 30, 1899. Ernest Bailey, Geo. R. Cox and Walter T. Hey, York, England.

Strikes arc to surface of molten lead to vaporize it. Injects through hollow carbon electrode a mixture of steam, carbon dioxide and acetic acid vapors, whereby white lead is formed and collected in bags.

627,002. June 13, 1899. Carl Luckow, Cologne-Deutz, Germany.

Electrolyte consists of mixture of alkali metal chlorate and carbonate in proportion of four to one. The solutions are very dilute (1½ per cent). Carbon dioxide and water continuously supplied.

631,839. August 29, 1899. H. C. Woltereck, New York, N. Y.

Product of United States patent 589,801, may be improved in covering power by (1) maintaining the temperature of the electrolyte below 25° C.; (2) removing white lead from the field of electrolysis as rapidly as formed; (3) continuously filtering the solution and injecting the carbon dioxide employed to regenerate it into the clear filtrate. Electrolyte is cooled by circulating water through cathode.

644,779. March 6, 1900. Joseph W. Richards and Charles W. Roepper, Bethlehem, Pa.

Lead anodes in electrolyte consisting of 5 per cent solution of sodium sulphite and acetate in proportions of 1 to 40. With current density of 100 to 200 amperes per square meter anode surface, the acetate is electrolyzed, yielding carbon dioxide, and lead carbonate is precipitated mixed with hydrate derived from action of sulphite. A small quantity of potassium nitrate may be added to facilitate solution of anode. Other organic acids, tartaric, formic, may replace acetic.

675,455. June 4, 1901. J. B. Tibbits, Hoosick, N. Y.

Modifies the process of patent 414,935, to produce colored white lead. To produce a blue pigment, attaches strips of copper to the face of the lead anodes, the product consisting chiefly of lead and copper carbonate. The depth of color depends on the relative area of the lead and copper. To produce a purple or violet pigment, coats the surface of both electrodes with iodine and adds anilin-red to the electrolyte. Employs a rubber or glass tube with lateral arms having downwardly-opening perforations to introduce the carbon dioxide.

675,459. June 4, 1901. John A. Yunck, Hoosick, N. Y.

Apparatus for executing the process of patent 414,935. Cell, an air-tight vessel having supports in its upper portion from which depend alternate foraminous anodes and cathodes of lead. A vertical shaft with radial arms having oppositely inclined vanes is journaled in the vessel, to agitate the electrolyte. Carbon dioxide is introduced through perforated pipes at the bottom.

675,460. June 4, 1901, John A. Yunck, Hoosick, N. Y.

Closed cell with rotary agitator. Lead anode with a supplemental carbon anode; lead cathode. Electrolyte, a 10° Baumé solution of sodium or ammonium nitrate, to each gallon of which is added one ounce of oxalic acid or sodium or potassium oxalate.

675,555. June 4, 1901, E. D. Chaplin, Winchester, and Henry G. Halloran, Boston, Mass.

Cell comprises a containing vessel with conical bottom and an inner porous cup. Anodes, lead pigs in the outer vessel around the porous cup. Cathode, a horizontal copper plate in the lower part of the porous cup. A hot solution of sodium or potassium nitrate or acetate fills both compartments, some sodium chloride being added to the anode compartment. The lead dissolves and is converted into chloride, which dissolves in the hot electrolyte and is gradually converted into oxychloride, which remains in solution. An alkali carbonate is added to the hot solution, precipitating the white lead. The caustic soda overflows from the cathode compartment and is carbonated, and the carbonate used for precipitating the white lead.

Dyes and Pigments.

256,330. April 11, 1882, Edward D. Kendall, Brooklyn, N. Y.

Produces aniline and toluine from the corresponding nitro-derivatives of coal-tar hydrocarbons. For example, places one part of nitro-benzine, or one part of a mixture of the same and nitro-toluine, in a porous cup with a mixture of water, thirty parts, and sulphuric or other acid or salt, two parts. The porous cup is placed in a solution of acidulated water, containing a carbon anode at each side of the cup. A carbon cathode, which may be covered with perforated cloth, extends to the bottom of the porous cup and is vertically reciprocated therein, thus effecting the reduction of the nitro body by hydrogen. May subsequently electrolytically oxidize the aniline or toluine or both, in a mixture of sulphuric acid and water, to a rose red, dark blue or green dye, by placing them in a porous cup with a carbon anode opposed to carbon cathodes outside.

294,051. February 26, 1884. J. K. Kessler, Milwaukee, Wis.

Cell, a vessel of wood having a transverse vertical partition at the middle, extending from the bottom part way to the top of the cell. Anode, blocks of copper at one side of the partition; cathode, a vertical sheet of copper at the other side of the partition. Electrolyte, a sodium chloride solution covering the partition. A cuprous chloride solution forms and settles to the bottom of the anode compartment and is drawn off and mixed with the caustic soda solution drawn from the cathode compartment to produce cuprous hydrate. The partition may be omitted, allowing the mixture to occur in the cell. The cuprous hydrate may be converted into suboxide by heating it to 100° C. or running boiling water through it. It may be converted into basic copper acetate by mixing it with neutral copper acetate, or into neutral copper acetate by mixing it with acetic acid.

(*To be continued.*)